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THE EFFECT OF TOTAL WATER REUSE AND ALUM CONTROL ON FIRST PASS RETENTION

by

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Product quality deterioration, caused by poor wet end control and the resulting build up of dissolved inorganic and organic contaminants, has hampered achieving complete water reuse in paper manufacturing. By using pulp-derived dissolved organic material, the study makes use of a dynamic retention/drainage jar to show the negative effects of these compounds on retention. Alum control is investigated as a means of improving retention in closed whitewater systems through literature review and experimentation.

A retention control strategy for total water reuse is proposed. It is based on the measurement and manipulation of alum concentrations in the stock chest; in low shear systems where no polymer is used, to control the electrokinetic balance for proper coagulation, and in high shear systems where polymers are used to eliminate the negative effects due to alum/polymer interactions.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the selected pollutional impacts on our environment and even on our health often require new and improved methodologies that will meet these needs both efficiently and economically.

This project investigated wet end chemistry relationships during the production of fine paper with a totally closed whitewater system. A strategy, based on the measurement and manipulation of alum (aluminum sulfate), is postulated as a means of improving paper quality and machine operation. Researchers involved with papermaking process optimization in closed whitewater systems should find the information contained in the report particularly useful. The Food and Wood Products Branch of the Industrial Pollution Control Division can be contacted for further information on this subject.

David G. Stephan
Director
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ABSTRACT

The escalating cost of raw materials, coupled with more stringent effluent limitations, have lead the papermaker to consider wet end chemistry optimization as a solution to these problems. They have also become aware of the possible benefits to be derived from increased whitewater reuse. While certain construction paper and paperboard manufacturers have used total water reuse to solve their problems, other categories of paper manufacturing have not been so successful. Product quality deterioration, caused by poor wet end control and the resulting build up of dissolved inorganic and organic contaminants, have hampered achieving complete water reuse. A previous study at Miami University, dealing with fine paper complete water reuse, cited the control of first pass retention as being the key to a successful total water reuse strategy.

By using pulp-derived dissolved organic material as a variable, the current study makes use of a dynamic retention/drainage jar to show the negative effects of these compounds on retention. The negative effects can be overcome by controlling the alum concentration to satisfy the cationic demand which this material exhibits. Excessively high alum concentrations, however, are shown in the study to decrease retention in a system where a high molecular weight cationic polymer was used. Controlling alum concentrations will reduce the negative effects of dissolved organics in closed systems and achieve maximum efficiency from costly polymer retention aids.

Interferences to the alum titration technique for measuring alum in whitewater samples were investigated. Iron and pulp-derived organic material were found to interfere slightly with the method causing higher results than the actual alum concentration in the sample. However, the method was found to be suitable for control purposes.

Various levels of pulp-derived organic material tended to hold zeta potential at zero over a wide range of alum concentrations. This phenomenon occurred at organic concentrations above approximately 200 ppm. This factor should be taken into consideration when using zeta potential as a wet end optimization parameter.

A retention control strategy for total water reuse is proposed. It is based on the measurement and manipulation of alum concentrations in the stock chest; in low shear systems where no polymer is used - to control the electrokinetic balance for proper coagulation, and in high shear systems where polymers are used - to eliminate the negative effects due to alum/polymer interactions.

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ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

A -- angstrom
CCS -- cubic centimeters per second
cm -- centimeter
CSF -- Canadian Standard Freeness
DRDJ -- Dynamic Retention/Drainage Jar
FPAR -- First Pass Ash Retention
FPFR -- First Pass Fines Retention
FTU -- Formazin Turbidity Units
gm -- gram
g/m^2 -- grams per square meter
HBAL -- Headbox Alum
HBC -- Headbox Consistency
HBF -- Headbox Fines
HBpH -- Headbox pH
HBT -- Headbox Temperature
kg -- kilogram
KPa -- kilopascal
$Kpam^2/g$ -- kilopascal-square meter per gram
M -- molar
mg -- milligram
mls -- milliliters
mm -- millimeter
mV -- millivolt
Nm/g -- Newton meters per gram
ppm -- parts per million
rpm -- revolutions per minute
SCAL -- Stock Chest Alum
SFU -- Sheffield Units
TAPPI -- Technical Association of the Pulp and Paper Industry
TOC -- Total Organic Carbon
TRAL -- Tray Alum
TRC -- Tray Consistency
TREM -- Tray Electrophoretic Mobility
TRF -- Tray Fines
TRSC -- Tray Specific Conductance
TRTB -- Tray Turbidity
ZP -- Zeta Potential

SYMBOLS

ug/ml -- micrograms per milliliter
um -- micrometers
umhos -- micromhos

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SECTION 1

INTRODUCTION

The pulp and paper industry is currently facing the implementation of stricter effluent limitations being proposed by the U. S. Environmental Protection Agency. By 1984, the industry will be required to reduce their effluent discharge of Biochemical Oxygen Demand and Total Suspended Solids from current levels. In meeting the previous Best Practicable Treatment Technology regulations, industry environmentalists recognized the cost-effectiveness of in-process recycle/reuse techniques for reducing effluent loadings. In fact, many mills in several subcategories of the industry have implemented total water reuse strategies for the complete elimination of their discharge. It is the purpose of this research to investigate the possibility of total water reuse in the non-integrated fine paper subcategory, specifically the manufacture of a high opacity offset grade.

Miami University investigated a totally closed whitewater system during the production of an offset grade in 1977 (1). The build up of dissolved and suspended solids in the whitewater system was monitored over a 96 hour period. Paper samples were collected at regular intervals during the trial and various quality analyses were performed. The study concluded that problems would arise in the areas of sizing, brightness reversion, and first pass retention. The authors recommended that these problems could be controlled by optimizing wet end chemistry, thereby controlling first pass retention. By computer simulation, they observed that this strategy would, in turn, eliminate the sizing and brightness reversion problems. The key is controlling retention.

In the study of retention, many authors have observed adverse effects associated with the build up of dissolved organic and inorganic substances. Swanson, Stratton, and Huettner (2), Lindstrom, et al (3), Arnson (4), and Penniman (5) have shown how small amounts of dissolved organic material can decrease the effectiveness of cationic retention aids. These dissolved materials can be lignin, hemicellulose, fatty and resin acids, or lignosulfonic acids. Their presence in the papermaking system causes a higher cationic demand thereby increasing the amount of cationic retention aid required to reach optimum flocculation. Alexander and Dobbins (6), and Heller, Scott, and Springer (1) have shown how dissolved inorganic materials build up in closed whitewater systems. According to classical electrokinetic theory, this phenomenon would decrease the amount of cationic retention aid required to reach optimum flocculation. This was shown to be true by Unbehend (7) using monovalent and divalent cations, such as sodium chloride and magnesium chloride.

Dissolved organic and inorganic materials in the system can be considered controlled or uncontrolled variables from a process control standpoint. Those materials coming into the system from the raw water or raw materials are generally considered not controllable. A process control variable such as alum, however, may become uncontrolled in a closed system. That is, if the concentration of alum in the system is not closely watched, a situation may develop where retention is adversely affected. Avery (8) demonstrated this by decreasing the alum concentration in a system using cationic starch. Retention on the machine was significantly improved. This same phenomenon has also been shown to occur with synthetic organic retention aids. Excessive amounts of these retention aids in the system will also cause stock dispersion and poorer retention (9).

It becomes increasingly clear from the previous discussion that the control of retention will become more complicated in a total closed system. In the 1977 machine trial at Miami University, dissolved organic and inorganic solids, as well as alum, continued to build up during the run. Based on this information, the objectives of the current study are: to determine how the alum demand changes under wet end conditions found in a totally closed system; to determine if the higher concentrations of dissolved organic and inorganic solids will interfere with the alum titration measurement technique; and to investigate alum control as a technique to improve retention in a totally closed system.

SECTION 2

CONCLUSIONS

From a retention point of view, the following conclusions can be drawn from this study:

1. In a totally closed system, some means of controlling the alum concentration will be necessary. This will involve measuring the concentration of alum prior to its point of addition, and making adjustments to the addition rate to maintain the proper quantity of alum in the system. The optimum alum level will vary with system conditions.

2. In a totally closed system, the build up of dissolved organic and inorganic compounds may or may not adversely affect retention depending on the relative concentration of each. The negative effects of increasing organic concentrations can be overcome by properly adjusting the alum level, or they may be overcome if other inorganics build up in the system in appropriate amounts. The particular organic/inorganic balance in the system should be recognized prior to alum addition. Zeta potential may be measured for this purpose if organic concentrations are not excessively high.

3. When using zeta potential as retention optimization parameter, the papermaker should be careful not to equate a zero reading with optimum conditions in the wet end. The level of dissolved pulp-derived material has a significant effect on the measurement of that parameter and may cause a false interpretation of where the optimum alum concentration occurs.

4. At high shear levels, polymer retention aids will be required to achieve satisfactory retention. Computer simulation of the data collected during the 1977 machine trial at Miami University predicted 25% ash retention as being satisfactory. Ash retention levels at medium and high shear levels during the current study were below 25%. Alum levels in polymer systems should be closely watched, especially where cationic polymers are being used, to achieve maximum retention benefits, based on the data collected during this study.

5. For control purposes, the alum titration, using a fluoride selective-ion electrode, is sufficiently accurate based on the variables considered during this study. The papermaker should be aware of possible interferences in their particular system and screen any additives for possible interference to allow proper interpretation of results from the titration.

SECTION 3

RECOMMENDATIONS

The problem of how to operate a fine paper manufacturing process effluent-free deserves added attention. Based upon information in the literature and added information obtained from this study, the following recommendations for additional research should be pursued:

1. A small section of the current study dealt with the interaction of alum with high molecular weight cationic polymer retention aids. Additional work should be performed to evaluate the use of cationic, anionic, and nonionic retention aids in closed mill systems, and to develop a strategy for their use.

2. Arnson (10), in his work investigating aluminum adsorption on cellulosic fibers, showed a definite pH/concentration dependence. His work, however, did not relate aluminum adsorption and retention. This work should be continued using the dynamic retention/drainage jar to relate aluminum adsorption at different concentrations and pH, with retention both with and without the use of polymers.

3. During this study, it was determined that sulfate ions produce a situation at pH 4.5 where the system is electrokinetically buffered in the proper range for coagulation to take place. This occurred even at extremely high alum concentrations. While not a dire consequence in systems where alum is the only retention aid, it could cause problems in systems using polymer retention aids, especially cationic polymer. The effect of sulfate on cationic polymer retention aids should be investigated with the focus on the consequences of sulfate ion build up in closed systems where these retention aids are used.

4. There is currently a great deal of interest in converting fine paper manufacturing from an acid process to an alkaline process. Alkaline paper is being promoted by the Library of Congress and commercial publishing firms because of the higher strength properties and superior ageing characteristics. Because of this movement in the industry, an attempt at operating an alkaline system totally closed should be made. It is claimed to be a "cleaner" system and, therefore, may be easier to operate in a closed fashion.

5. Other interferences to the fluoride selective-ion electrode technique for measuring alum concentrations should be investigated. Polymer retention aids and pigment extenders have been mentioned as possible interfering compounds. A modest experimental program could clarify this issue.

SECTION 4

LITERATURE REVIEW

BACKGROUND INFORMATION

Concern over fines fraction retention in paper manufacture has accelerated in recent years. Increasing government restrictions on waste water discharges, coupled with the rising costs of all raw materials, represent an economic double loss. The fine solids which are not appearing in the final product are also costly to remove in effluent treatment processes. Much research has been initiated to respond to this challenge by investigating the control of retention during sheet formation.

In the study of retention, there are basically two schools of thought. The first is to ignore first pass retention and rely on recovery and recirculation of white water to achieve satisfactory overall retention. The second is to emphasize improvement in first pass retention by physical or chemical manipulations of the wet-end to the point that the recovery system has only minor quantities of fines to recover (11). Current practice in the industry is generally to follow the first school of thought, consequently leading to a build up of fines in the headbox system. Under the conditions of total water reuse, this practice will have to cease. Problems associated with fines are magnified with increasing degrees of closure. As demonstrated by a totally closed machine run at Miami University in 1977, the build up of ash in the headbox caused by poor first pass retention was associated with problems in color control, brightness reversion and sizing. Future control strategies will have to be directed at optimizing first pass retention.

Besides direct economical reasons, there are a number of other reasons for optimizing first pass retention (12). These are:

1. The build up of fines retards drainage. Fines are the direct reason for low freeness which causes decreased production rates.

2. Felt filling is caused by a heavy load of fines. The advantages of long lasting, bacterially inert modern fiber felts will be overshadowed by their vulnerability to filling by fines.

3. Two-sidedness of the sheet will be a problem in systems loaded with fines and where the retention mechanism is primarily mechanical filtration.

4. The high surface area of the fines fraction in the stock will adsorb more than its share of chemical additives such as size, wet strength resins, internal bonders, and dyes.

5. A build up of fines will cause a dirty system. Pitch and slime are associated with systems loaded with fines. Softwood full-chemical pulps are low in fines but these fines contain ray cells where resin and fatty acids are found. The cells (from sulfite pulp) are recognized to be the source of pitch trouble on the machine (13). Because of the generally higher extractives and color body content of the fines fraction, loss of brightness on aging has been attributed to their presence (14).

FINES FRACTION DEFINITION

Before proceeding to describe the mechanisms of fines retention, it would be important to define what is meant by "fines" or "fines fraction". Using conventional pulp fractionation procedures such as the Bauer-McNett and Clark multi-screen classifier, the fines fraction is defined as that fraction which passes the last screen, usually 200 mesh (TAPPI Standard T-233). Britt (15) described a procedure developed at the SUNY College of Environmental Science and Forestry for fines fractionation using a 200 mesh Tyler screen with holes 76 um in diameter. It is generally accepted that particles passing through this screen are the fines fraction. In a paper machine whitewater system, this fraction would also include inorganic or filler fines and pigments. The particle size of fillers commonly used in the industry is in the 0.25 to 2.5 um range.

Table 1 (16) shows the fines fraction of a number of headbox samples from commercial machines.

TABLE 1. FINES FRACTION - VARIOUS COMMERCIAL MACHINES (16)

Paper Grade	Fines Fraction %	Ash %
1. Top Liner Kraft	20.9	Nil
2. Waxing Base, glassine plus filler	49.4	13.2
3. Book, machine coated (a)	54.0	17.8
4. Book, machine coated (b)	66.9	34.7
5. News grade with filler	65.7	39.7
6. Newsprint, no filler	42.9	Nil
7. Reproduction grade	35.8	10.2
8. Bond grade	38.7	Not available
9. Tissue	71.9	Nil

This data shows that even for long fibered virgin pulp and no filler (line 1), there is a considerable build up of fines. A maximum is reached at 71.9% with tissue paper showing the adverse effects of high machine speed and low basis weight on retention.

All stock samples can be partitioned into three fractions: the fiber fraction - those particles not passing a 200 mesh screen; the organic material (fiber fines) passing the 200 mesh screen; and the inorganic material (filler pigments) passing the 200 mesh screen. The latter two fractions are considered together as the fines fraction. These definitions shall be used for the remainder of this report.

MECHANISMS OF RETENTION

There are basically two forces involved in the retention of fines in a papermaking system: hydromechanical and colloidal. Hydromechanical forces include the mechanisms of sieving and entrapment and, while it is not always practical to control these mechanisms to any great extent on a given machine, there are several mechanical modifications that will improve retention. Colloidal forces of retention relate to the electrokinetic potential between particles and it is here that attempts are made to manipulate retention in practice.

In a papermaking system, the mat is formed by passing a fiber suspension over a wire mesh to filter or separate the fiber from the liquid medium. Fibers which are 500-4000 um long and 20-100 um wide form about 2-100 layers thick in a three dimensional network (17). In the first layer are large fibers which in turn collect finer and finer fibers as the pore size decreases.

Each layer of fibers captures a portion of the free particles depending on the diffusion rate, i.e., the number of particle-fiber collisions. This diffusion process is predicted by the following relationship (18):

$$\ln(W_o/W_h) = 4\alpha Eh/D_f$$

where W_o = weight of particles fed to mat (g)

$W_h = W_o - W_{mat}$ = weight of particles passing thru mat (g)

W_{mat} = weight of particles retained by the mat (g)

h = mat height (cm)

D_f = fiber diameter (cm)

α = mat solid fraction (dimensionless)

E = the effective fiber collection efficiency, is the ratio of the number of particles collected by the fiber per unit time to the number of particles in the fluid stream passing through an area equal to the projected area of the fiber, per unit time.

Rearranging the above expression in terms of W_h you obtain:

$$W_h = \frac{W_o}{e^{4\alpha Eh/D_f}}$$

From this expression, it is easy to see that, in order to improve retention, i.e., decrease the weight of the particles passing through the mat, several parameters may be varied. The mat solid fraction (α), the fiber collection efficiency (E), and the mat height (h) may be increased, or the fiber diameter (D_f) may be decreased to improve retention. For all practical purposes, with a given papermaking system and furnish W_o, α, h, and D_f are constant and retention varies according to the E term. Collection efficiency is manipulated chemically as will be discussed later.

Superimposed on this diffusion mechamism of retention are forces which tend to wash fines out of the fiber mat. Turbulence in the headbox and slice necessary for proper fiber dispersion also cause conditions which obviate proper retention of fines in the first 5-20% of the wet-end. It is in this portion of the machine where more than half of the total loss of fines through the wire occurs (19). Compression and relaxation cycles caused by table rolls also take their toll in washing fines from the fiber mat. These forces cause a change in the distribution of fines in the mat to a point where fines will be lower in concentration on the wire side.

Retention by purely mechanical means is an inefficient process. Usually retention aids are used to enhance the colloidal forces so that realistic retention levels are achieved. In essence, mechanical modifications to improve retention require machine downtime and capital expenditures which may be impractical to implement; however, several such modifications will be discussed later. In practice, the colloidal forces are manipulated on any given machine to achieve satisfactory retention.

Coflocculation, or the interfacial forces of the particles which control colloidal flocculation have been found to be the major mechanism for retaining the fines fraction in the fiber mat (20). Coflocculation refers to the mechanisms of coagulation and flocculation.

The coalescence of colloidal particles or fines is a result of reducing the electrostatic forces of repulsion. Every solid, when placed in water, will develop a change at the surface due to three phenomena: the ionization of surface groups, the specific adsorption of ions from the solution, or by internal faults or defects in the crystal lattice which may leave a net positive or negative charge in the structure (21). Cellulose fibers have a negative charge due to ionization of the surface carboxyl groups, and, thus exhibit a negative zeta potential. Inorganic fillers and pigments are usually dispersed with a phosphate dispersing agent prior to mixing with the stock. Therefore, these particles exhibit a negative zeta potential (22). Zeta potential is a term used to define the relative repulsive forces between colloidal particles and is defined by the equation (23):

$$Z = \frac{4\pi\delta q}{D}$$

where Z = zeta potential

δ = thickness of the zone of influence of the charge on the particle

q = charge on the particle

D = dielectric constant of the liquid

Therefore, the goal for optimizing the coagulation mechanism in a papermaking system is to reduce the zeta potential to zero by reducing the charge on the particle, by reducing the thickness of the zone of influence of the charge on the particle, or by increasing the dielectric constant of the liquid.

The above relationship was first predicted by Helmholtz and Perrin in the late 1800's and was predicated by the theory that the boundary between solid and liquid phases contain layers of oppositely charged molecules. This is called the electric double layer and is represented in Figure 1 (24). Helmholtz and Perrin showed that the potential E varied linearly across the layer as a function of the double layer thickness, the surface charge density, and the dielectric constant of the liquid. In later experiments, this theory was shown to be unrealistic due to the thermal diffusional motion of ions and molecules in solution.

Gouy and Chapman predicted an electric double layer which consisted of a fixed potential determining ion layer and a diffuse layer of oppositely charged ions in solution. This predicted model is shown in Figure 2 (25). Mathematical representations of this model made by Kruyt lead to unrealistically high double layer capacities and ionic concentrations by failing to consider ionic dimensions (26).

Figure 1. Electric Double Layer by Helmholtz and Perrin (Ref 24., Copyright © 1975. TAPPI. Reprinted from D.G. Williams and J.W. Swanson, "Electrokinetics. Retention of Fine Solids During Paper Manufacture", TAPPI PRESS, Atlanta, 1975, p. 47, with permission).

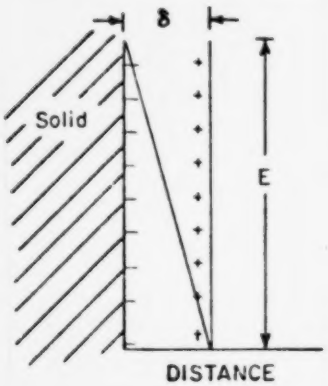
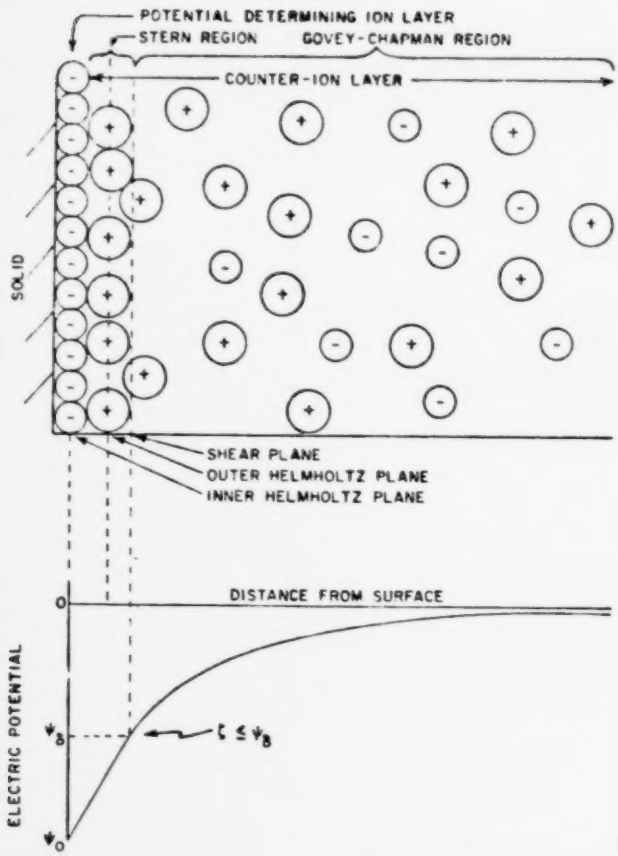


Figure 2. Electric Double Layer by Stern and Graham (Ref. 25, Copyright © 1975. TAPPI. Reprinted from D.G. Williams and J.W. Swanson, "Electrokinetics. Retention of Fine Solids During Paper Manufacture", TAPPI PRESS, Atlanta, 1975, p. 48, with permission).



Stern and Graham improved on the mathematical representation made by Kruyt by introducing ionic dimensions. Stern assumed that a layer on ions remained attached to the solid surface by electrostatic and physical forces characteristically particular to each ion and solid surface. In Figure 2, the electrochemical potential Ψ_o is comprised of the potential drop occurring over the immovable region and the electrokinetic or zeta potential occurring over the movable zone. Graham showed that the adsorbed ions are chemisorbed and partially dehydrated and that the cations remain hydrated and are attracted only by electrostatic forces. Their theories are shown in Figure 2 where Graham refers to the Inner and Outer Helmholtz Planes.

Superimposed on the forces of repulsion between particles are the attractive residual valence forces called London-Van der Waal's forces. These attractive forces exist between all particles of colloidal size ($1x10^{-4}$ to $1x10^{-7}$ cm diameter) and vary inversely as the square of the separation distance at distances of a few angstroms, and vary inversely as the fourth power of the separation distance at large separation distances up to several hundred angstroms. London-Van der Waal's forces are represented as curve 7 in Figure 3 (27). Curve 1 in Figure 3 represents the experimental function of the separation distance predicted by Derjaguin, Landau, Verwey, Overbeck (DLVO). The DLVO theory states a relationship between the free energy of the double layer and the ionic composition of the dispersion medium. It shows overlapping electrical double layers increase the repulsion energy when two particles approach one another. Curves 2 through 6 represent the net potential energy between particles under increasing electrolyte concentration or counterion valence. The curves show that if two particles have sufficient kinetic energy as they approach one another to get over the repulsive energy barrier, the attractive forces will take over and the particles will coalesce.

According to the theories of coagulation, the Stern and zeta potentials are equal and this behavior has been shown to be true for quartz sols and titanium dioxide sols. Although the exact position of the slip plane in the diffuse layer is not known, lending the zeta potential inaccurate as to the quantitative measurement of the stability of a sol, some functional relationships between zeta potential and the net potential of interaction between colloidal particles have been made. General experience with correlating zeta potential with the degree of stability of a sol is supported by the DLVO theory (28).

All of the theories discussed predict two methods by which repulsion between colloidal particles may be reduced: by reducing the surface charge through a change in pH or through introduction of an ion of opposite charge which is adsorbed, or by compressing the diffuse layer of counterions by introducing more counterions in the solution. In regard to pH control, Arnson (10) has shown that the majority of surface carboxyl groups on the cellulose are ionized at pH 4 and very little change occurs in the pH 4 to pH 5 region. Since

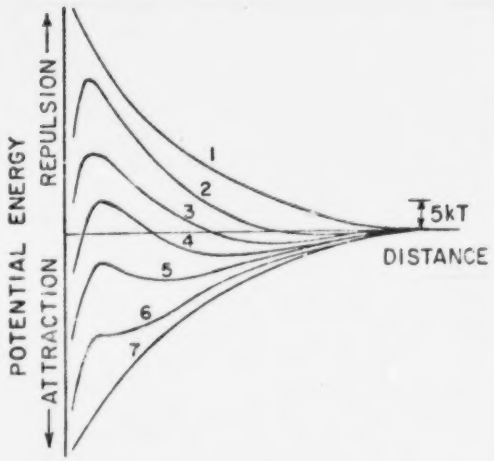


Figure 3. Net Potential Energy of Interaction Between Colloidal Particles (Ref. 27, Copyright © 1975. TAPPI. Reprinted from "Electrokinetics Retention of Fine Solids During Paper Manufacture", TAPPI PRESS, Atlanta, 1975, p. 48, with permission).

this is where most alum-rosin systems operate, pH control would not be effective in changing surface charge. To reduce the repulsion by compressing the diffuse layer, the Schulze-Hardy rule states that the amount of counterions necessary to eliminate a net repulsion is proportioned to the inverse sixth power of its valence. Therefore, much less trivalent cation compared to monovalent cation would be required to achieve satisfactory coagulation.

Flocculation is characterized by the adsorption of a polymer molecule onto the surfaces of two or more particles, bridging them together to form a matrix. The stability of this matrix or floc varies with the amount of turbulence (hydraulic shear) in the system. Those polymers forming tenacious flocs are relatively long-chain high molecular weight organic polymers and are more effective in retaining fines under turbulent conditions than the relatively short chain low molecular weight polymers. Britt (29) called these flocs "hard" and "soft" depending on their relative abilities to improve the retention of fines under conditions of high hydraulic shear. The high levels of retention obtained by hard flocs are not necessarily good. High retention can be accompanied by nonuniform formation, inefficient pigment utilization and drainage problems.

The best examples of soft flocs are those produced by the addition of salts to the system. Flocs are formed by the same mechanisms discussed earlier for coagulation and represent the classic Shultz-Hardy series showing the increasing coagulating power with increasing cation valence. Unbehend (30) demonstrated this using a dynamic retention/drainage jar. His data shows that all salt flocs are turbulence dependent and retention tends to be the same at 1600 rpm. Unbehend also demonstrated the effect of redispersion on the surface interactions at a given level of turbulence and showed that there was a negligible effect.

Flocculation equilibrium was dependent on the given level of turbulence.

Similar retention analyses were performed by Unbehend with two low molecular weight cationic polyelectrolytes (polyethylene imine - PEI) havig molecular weights of approximately 50,000 and 6,000. The addition of these polymers showed a considerable increase in floc tenacity over the blank with the higher molecular weight polymer being more effective. Redispersion of the flocs demonstrated that the higher molecular weight PEI had a lower ability to reflocculate to the same level of retention. Molecular weight or chain length of the flocculent appears to have the greatest effect on reformation.

Hard flocs are generally formed by the addition of high molecular weight organic polymers to the papermaking system. Very high levels of retention can be obtained. Successive redispersions, however, reduce floc tenacity and lower retention.

Unbehend postulated a mechanism similar to that of Goossens and Luner (31) describing the patch-spreading concept to explain the phenomenon of decreased retention with each dispersion for the high molecular weight polymers. Redispersion causes the polymer to remain on the surface to which it is most strongly adsorbed. Hydrodynamic forces spread the polymer to form a patch with a flatter appearance. Since the loops do not then extend into the solution subsequent flocculation occurs through electrostatic attraction forming a soft floc with its lower retention value.

FACTORS AFFECTING RETENTION

Alum

Alum is used in the production of fine paper for three purposes: to control pH, to precipitate rosin size, and to increase retention. Varying levels of alum can be used to optimize any of the three parameters. Usually, a compromise is reached in favor of the parameter more easily measured. By this theory, it is wise to control pH independently and to stress sizing over retention as the major use of alum. Polymeric retention aids would then be used to optimize retention at a given pH and alum level (32).

There are a number of reasons why alum is an important factor in affecting retention. Alum dissociates in water to aluminum ion and sulfate ion. Aluminum ion has a high charge density (+3 for a radius of 0.57 Å) which gives the ion its chemical personality. It has a natural tendency to reduce its charge density by increasing the size of the charged species, by complexing with others which are neutral, or by decreasing the net electrical charge by complexing with other species of opposite charge. Aluminum characteristically forms an octahedral complex by coordinating with six other groups. The ligands represent negatively charged or neutral compounds. These ligands may be the rosinate ion, sulfate ion, hydroxyl ion, or water.

Depending on pH, aluminum may be present in various forms having different adsorptive characteristics which will be discussed later.

In practice, alum will enhance retention by compressing the electrical double layer of the colloidal particles, and/or complexing with negatively charged ions in the solution to facilitate coagulation, and by polymerizing to form a bridge between particles to form a flocced structure.

pH

Besides controlling the structure of alumina, pH will also affect retention by influencing the zeta potential. The lower the pH, the more positive the zeta potential. The hydrogen ion acts to suppress the ionization of carboxylic acid groups in the hemicelluloses and phenolic hydroxyl groups in the lignin (33).

Dissolved Organics

Huettner (2) postulated that soluble organics will build up in the papermaking system with increasing degrees of closure. He extracted hemicellulose from wood pulp and put it back into a furnish while observing retention. Hemicellulose as low as a tenth of a percent on fiber decreased retention from 78% to 46% in an alum pulp system.

Lindstrom, et. al. (3) showed the effects of wood-based polymers on the flocculation of suspended solids. Increasing concentrations of pine xylan increased the amount of polyacrylamide needed for flocculation. The same effect was shown for increasing concentrations of lignosulfonic acid.

Arnson (4), in his work with polyelectrolyte retention aids, showed the negative effects of soluble materials commonly found in white water of unbleached Kraft papermaking systems. These soluble materials include lignin, hemicelluloses, fatty and resin acids, and many inorganic salts. Further work by Arnson showed that a decrease in retention was caused by the interaction of soluble negatively charged organic material with the cationic polyelectrolyte decreasing its effectiveness as a retention aid.

Dissolved Inorganics

As stated in the previous section on coagulation, even monovalent cations such as sodium will cause an increase in retention by reducing the zone of influence of the negatively charged colloid. The zeta potential is, thereby, reduced and coagulation is enhanced. Similar effects are caused by multivalent cations with trivalent cations such as aluminum and iron being most effective.

Besides the positive effects of multivalent cations in solution, there are several negative effects which will cause a decrease in retention. Divalent and trivalent ions, introduced as hardness in the water supply, will compete with cationic polyelectrolyte retention aids for available adsorption sites. Therefore, retention will suffer. The theory of maximum retention at zero zeta potential might not apply in this case since more polyelectrolyte would be required than in pure water. Maximum flocculation might occur at +5 or +10 mv under these circumstances (34). In addition, the increase in positively charged ions in the system will cause a cationic retention aid to coil due to the electrical charge repulsion.

One of the most common inorganic anions in a typical papermaking system is the sulfate ion. Sulfate is introduced with the aluminum ion as aluminum sulfate ($Al_2(SO_4)_3 \cdot 14H_2O$), commonly known as papermakers alum. Since sulfate is "nonsubstantive", it tends to build up and may reach very high concentrations depending upon the degree of closure of the system (6). Sulfate has a negative effect on retention by reducing by two units the cationic charge of the +3 alumina complex. High concentrations of sulfate will shift the equilibrium in the system which will result in the predominance of the alumina/sulfate complex. This complex is less effective as a coagulant and, therefore, retention will suffer.

Types of Additives

Most fillers used in the paper industry range from 0.25 microns to 2.5 microns and show differences in their ability to be retained. Beazley (35), in referring to previous work by Brecht and Pfrezschner, showed that retention goes through a maximum depending upon the relation between mechanical filtration and chemical adsorption. Figure 4 graphically illustrates this using prepared particle size fractions of various minerals. In addition, these fillers also vary in their observed zeta potential in tap water. This variation may affect the retention observed in the papermaking system according to the electrical environment during formation.

Starch is one of the most widely used chemical additives in the papermaking process and can be the source of a retention problem. Huettner (36) showed that oxidized starch contributed by coated broke might cause retention to drop to near zero. Oxidized starch added to a system from 0% to 2% caused a decrease in retention from 78% to 8%. Increasing the alum concentration one-hundredfold did not improve retention. The ability of starches to form a stable complex with fine particles explains the reason for the lack of effectiveness of alum to solve the problem.

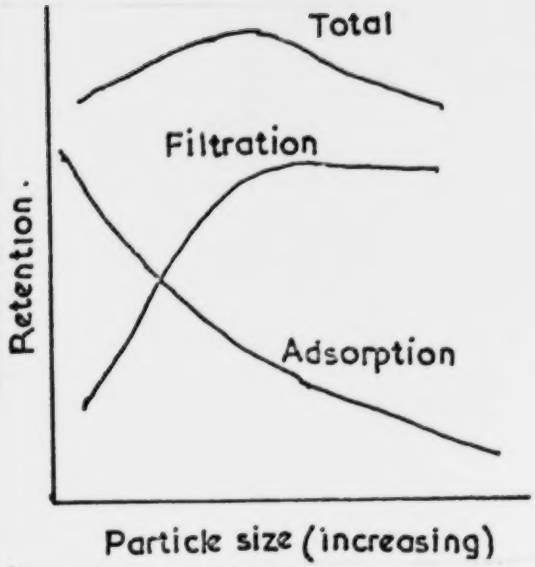


Figure 4. Retention vs. Particle Size (Ref. 35, Copyright © 1975. TAPPI. Reprinted from K.M. Beazley, "Filler Pigments. Retention of Fine Solids During Paper Manufacture", TAPPI PRESS, Atlanta, 1975, p. 104, with permission).

CLOSED SYSTEM CONDITIONS

Heller, Scott, and Springer (1) reported on the operation of a pilot paper machine at Miami University in 1977 which documented the negative effects of system disclosure on the first pass retention. This pilot fourdrinier machine, producing a high opacity offset paper, was run totally closed for four days. Ash, acidity, chloride, sulfate, and polyvalent cations, as well as first pass retention, were monitored throughout the run. The data was fit to first order equations and extrapolated by computer to equilibrium concentrations. Problems were predicted and observed in the areas of first pass retention, sizing, and sheet aging properties.

First pass retention of clay and TiO_2 was observed to decrease from 53.5% and 75.8% to 24.0% and 34.5%, respectively, during the four day run. Ash equilibrium first pass retention was predicted to be 13.6%.

The results of the computer simulation of the run predicted that the problems associated with this closed system could be eliminated by keeping the first pass retention of ash above 25%.

A number of factors contributed to the low retention values which were observed in the system described above. There was an apparent charge reversal on the fine particles which is documented by the steadily increasing zeta potential from +8 mv to +14 mv. This increase in positive charge in the system is not excessive; however, it does indicate movement away from the isoelectric point - theoretically, a point where

optimum coagulation should occur. In addition, a cationic polyelectrolyte retention aid was being used which would also cause the observed zeta potential to increase. While the measurement of zeta potential and its correlation to the optimum conditions for best first pass retention is not well established in a system using retention aids, the observed trend towards a more positive system would produce less than optimum retention levels. There was a substantial increase in the sulfate ion concentration in the system. Sulfate will form a complex with the aluminum ion thereby reducing the charge of that alumina species and hindering its effectiveness as a coagulant and retention aid. The level of volatile dissolved solids, i.e., dissolved organic material, increased to approximately 800 ppm by the end of the four day run. This concentration represents a 0.06% solution of this material. As previously stated, as little as 0.10% of hemicellulose would cause a 32% decrease in retention in an alum-pulp system. These observations would suggest that dissolved organics might be responsible for the decrease in retention which was observed.

WAYS TO IMPROVE RETENTION

As was discussed in the section on mechanisms of retention, there are basically two forces involved - mechanical forces and colloidal forces. Owing to this fact, there are two ways to manipulate retention on the wire. They are mechanical and chemical.

Mechanical

Several machine wet end modifications are available to the papermaker to improve first pass retention. On single wire formers, these modifications take the form of suction boxes, foils, or a combination of the two called vacufoils which are suction boxes with foil supports.

Forming a sheet on an open wire involves depositing a fiber suspension on top of the moving open wire. Filtration takes place using elements under the wire that create a vacuum. Traditionally, table rolls have been used almost exclusively for this purpose. This is a nip forming element that produces both a vacuum and a pressure. It is this pulsating action which produces turbulence and a washing out of fine solids from the sheet. Better formation and retention is obtained by devices producing a more mild vacuum.

Wet suction boxes were designed to have a low constant vacuum along their open areas and provide basically undisturbed drainage. A wet suction box has a slotted cover, or drilled cover, with an open area of between 50% and 90%. Vacuum is applied and controlled by a fan. These conditions create a very efficient drainage element for maintaining retention and reducing two-sidedness (37).

Foils are stationary elements with the front part supporting the wire and a trailing section diverging away from the wire forming a water filled nip. This nip creates a vacuum and by varying the angle, the length, and the curvature of the foil various vacuum profiles can be obtained. Compared to table rolls, foils produce a much longer and lower vacuum pulse, and can be placed closer together. Therefore, a foil table has a much higher drainage capacity than a table-roll table. Foils create a vacuum with discrete pulsations which vary in intensity according to machine speed. Since the geometry of the foils can be changed and the pulses controlled, the drainage capacity and disturbance levels can be adjusted accordingly.

Vacuum foils are basically wet suction boxes with foils substituted for the flat surface. This creates a dynamic suction pulse which disturbs the web more than ordinary wet suction boxes. Vacuum foils give a retention and filler distribution which lies between the wet suction boxes and the foils themselves.

More uniform distribution is apparent by using foils and wet suction boxes. Because of the low drainage capacity, high disturbance level, low retention and excessive two-sidedness, table rolls are rapidly being replaced by these other vacuum producing elements.

In practice, a papermaker trying to manipulate first pass retention on a given machine may be forced to disregard improvements possible by mechanical modifications due to lack of capital. Manipulating the typical machine operating variables such as refining, machine speed, angle of impingement of the jet on the wire, or consistency may not achieve adequate retention. If this is the case, it will be much more important to consider manipulating the colloidal aspects of retention by chemical means to achieve the desired results.

Chemical

There are essentially three chemical variables available to optimize the coflocculation of fines in an alum-rosin sized system where fine paper is being produced. Those variables are alum, pH, and retention aid.

Alum is one of the most widely used chemicals in the paper industry. Its utility comes from the fact that it is used for a variety of purposes including alum-rosin sizing, pH control, pitch control, curing of wet strength resins, and the retention of non-fiberous additives. For the mechanism of retention and the adsorption of aluminum to the pulp fines, fiber, and non-fiberous additives to be optimized, pH and alum concentration must be considered simultaneously. Arnson (10), in his work with aluminum chloride and aluminum sulfate, showed that adsorption of aluminum to cellulose was both pH and concentration dependent. Figure 5 shows his results with 2.5×10^{-4}M solutions of $AlCl_3$ and $Al_2(SO_4)_3$.

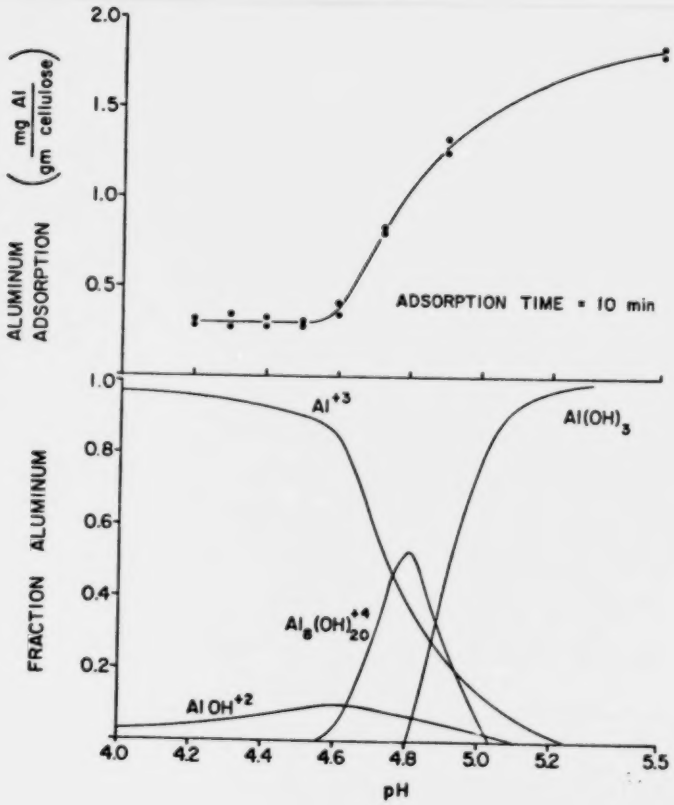


Figure 5. Aluminum Adsorption and Species Distribution as a Function of pH for $AlCl_3$ @2.5×10^{-4}M (Ref. 10, Reprinted with permission of The Institute of Paper Chemistry, Appleton, Wisconsin).

The figure shows the predominance of four aluminum species in solution. They are Al^{+3}, $AlOH^{+2}$, $Al_8(OH)_{20}^{+4}$ and $Al(OH)_3$. All are soluble with the exception of the insoluble $Al(OH)_3$ which forms a precipitate above pH 4.8. The sharp increase in aluminum adsorption which begins at pH 4.4 coincides with the formation of the cationic aluminum polymer $Al_8(OH)_{20}^{+4}$. Figure 6 shows the effect of increasing the concentrations of aluminum in solution on the pH range at which the $Al_8(OH)_{20}^{+4}$ species is present, and the point at which maximum adsorption of aluminum begins.

Arnson showed, through these analyses, that increasing the aluminum concentration will decrease the pH at which the adsorption of aluminum by cellulose rapidly accelerates.

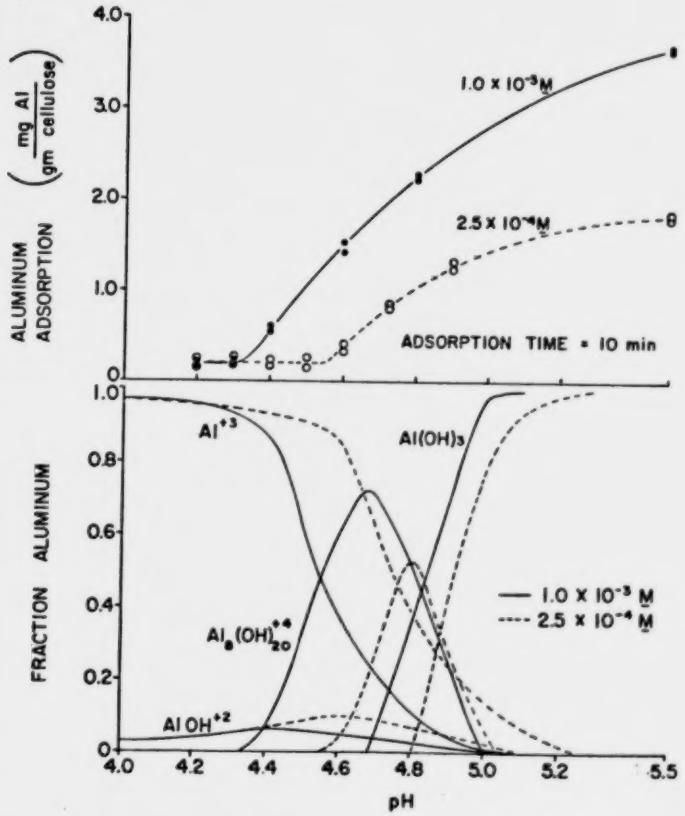


Figure 6. Aluminum Adsorption and Species Distribution as a Function of pH and Aluminum Concentration for $AlCl_3$ (Ref. 10, Reprinted with permission of The Institute of Paper Chemistry, Appleton, Wisconsin).

In differentiating the adsorption phenomenon of the various aluminum species, Arnson showed (Figure 7) the concentration independence of the Al^{+3} species. In terms of relative adsorption, only 5-10% of the total aluminum was adsorbed in the low pH region. In reality, a papermaker can expect very little aluminum to be adsorbed on the sheet when running at a low pH where the Al^{+3} species predominates.

Avery (8) discovered this to be the case in many systems where low pH caused the build up of aluminum in the whitewater. By controlling the aluminum concentration in the whitewater to the lowest practical level and running at a slightly higher pH, retention could be drastically improved. He also conducted laboratory studies which showed a strong

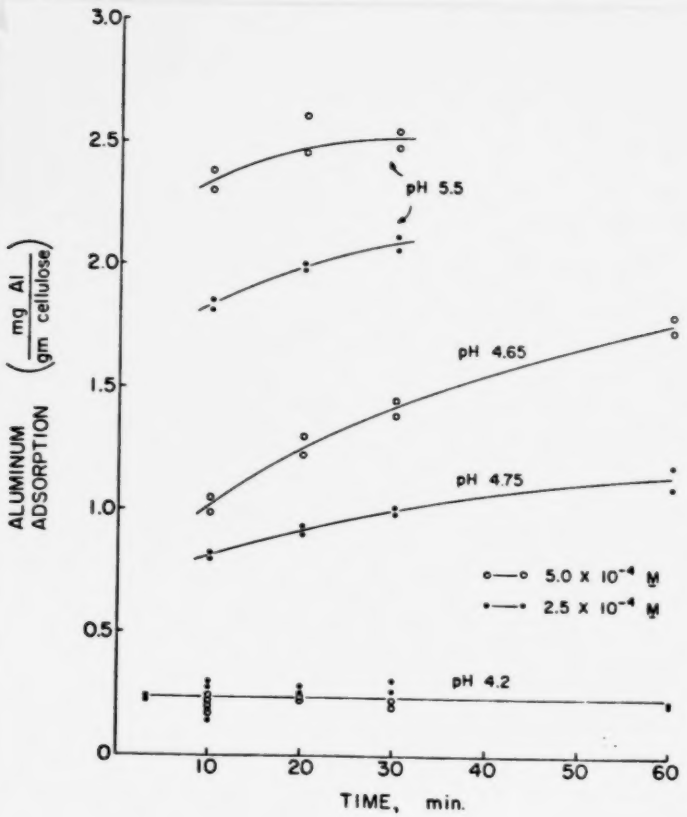


Figure 7. Aluminum Adsorption as a Function of pH, Time, and Aluminum Concentration for $AlCl_3$ (Ref. 10, Reprinted with permission of The Institute of Paper Chemistry).

alum-retention aid interaction such that increasing the alum concentration severely decreased the effectiveness of the retention aid. In his experiments, cationic, anionic, and nonionic polymers were used.

It should be noted that even though in Figure 7 the adsorption of aluminum continues to increase in the region where $Al(OH)_3$ predominates, controlling pH in that region should be avoided due to the build up of aluminum hydroxide precipitate which will occur. This material will accumulate on machine parts and cause maintenance problems if allowed to go unchecked, and may also adversely affect sizing.

Retention aids are another method to improve the retention of fines in a papermaking system. These polyelectrolytes may be inorganic, such as alum, or they may be organic, natural or synthetic. Polyelectrolytes have gained acceptance in recent years because of their ability to significantly improve the retention of costly nonfibrous additives when used in very small quantities without causing pH fluctuations.

Organic polyelectrolytes are polymers containing sufficiently charged functional groups to impart water solubility to the polymer and allow it to behave as an electrolyte. These are classified according to the type of charge which resides on the backbone of the polymer. Thus, there are nonionic, anionic, cationic, and amphoteric polyelectrolytes. Organic polymers also vary according to molecular weight. The combinations of molecular weight and charge form the basis for selecting a particular organic polyelectrolyte. Anionic polymers are normally used in acidic systems where alum is also being used (38).

LITERATURE REVIEW CONCLUSION

The overall goal of this research project was to begin the development of a strategy to achieve total water reuse while producing a saleable product. A review of the literature indicates that the control and optimization of retention is the key to implementing a successful water reuse strategy. The theory of retention and the empirical data supporting it suggest many effects and interactions which will affect retention in open or closed white water systems. These effects and interactions are summarized below:

1. Shear (Turbulence) - In all cases, shear and retention are inversely correlated with increasing shear causing decreasing retention. Shear is directly proportional to machine speed.

2. Alum - Little information exists on the effect of increasingly high levels of alum in polymer-free papermaking systems with respect to retention. Negative effects on paper properties, i.e., sizing and aging properties, have been documented. Alum forms "soft" shear-sensitive flocs resulting in poor retention in high shear systems. Alum also inhibits the effectiveness of some polymers when excessive amounts are found in the white water.

3. Dissolved Inorganics - Besides alumina, other ions exist in white water systems that are capable of improving retention. These ions are predominantly calcium, magnesium, iron, and manganese. They act to compress the electric double layer and reduce the repulsive forces which inhibit coagulation. Excessive amounts, however, may increase the repulsive forces in addition to reducing the effectiveness of polymer retention aids.

4. Dissolved Organics - Wood derived organic material has been shown to decrease retention in all cases, apparently through interaction with polymer retention aids. This material has been shown to build up in closed white water systems.

5. pH - The effect of pH is primarily due to its correlation with the particular hydrolysis species of the coagulant being used. In the case of alum, aluminum hydroxide is the species postulated as being responsible for improving retention, therefore controlling pH to allow the formation of this species is necessary.

6. Mechanical - Modifications to paper forming machinery are possible for improving retention; however, on a particular machine, manipulating mechanical effects on retention are not practical.

7. Temperature - Theory states that increasing temperature of the white water will improve retention by increasing particle collisions and enhancing coagulation. This effect will also increase the drainage rate. Little information exists on the specific effects of temperature on retention.

SECTION 5

EXPERIMENTAL DESIGN AND PROCEDURES

HYPOTHESIS

The experimental program is based on the premise, developed through a review of the literature, that the key to achieving successful in-process total water reuse is in optimizing the first pass retention of ash. A papermaker has three basic parameters to manipulate in optimizing retention. These are alum level, pH, and polymer type and level. The manipulation strategy suggested in the literature is based on the constant rate of alum for setting the rosin size, control of pH with an alternate acid, and polymer use to control retention. This strategy will not work in a totally closed system due to the accumulation of alum caused by incomplete retention on the wire. This leads to a build up of dissolved and suspended solids in the whitewater which also adversely affects retention and paper quality. It is the hypothesis of this research that, to achieve satisfactory total water reuse, close control of alum will be necessary.

OBJECTIVES

In order to develop a strategy for the control of alum, two things must be determined. First, the level at which alum is to be controlled must be determined, and second, the mechanics of how and where alum will be controlled on the paper machine must also be determined. To accomplish this, three specific objectives were formed. They are:

1. To determine how the alum demand of the system varies according to changes in wet end chemistry;

2. To investigate possible interferences to the alum titration technique for measuring alum in papermaking systems; and

3. To demonstrate an alum control strategy on a pilot scale fourdrinier machine and evaluate its effectiveness.

The experimental program is divided into three phases which correspond to the objectives listed above. The specific design and procedures used in each phase will be discussed independently below.

PHASE I - BENCH SCALE RETENTION ANALYSES

A series of bench top experiments were conducted to investigate the effect of dissolved organic and inorganic materials on the colloidal forces of retention to understand how the demand for alum will vary in a totally closed system. The apparatus used for these experiments is known as a Dynamic Retention/Drainage Jar (DRDJ).

Dynamic Retention/Drainage Jar

A procedure was developed at the Empire State Paper Research Institute which allows the measurement of the total amount of fines in a given stock system and the colloidal retention of these fines during and after exposure to given levels of turbulence. Figure 8 shows the device used for this procedure. TAPPI (Technical Association of the Pulp and Paper Industry) has a provisional method based on these procedures. (See TAPPI Method T261pm-79).

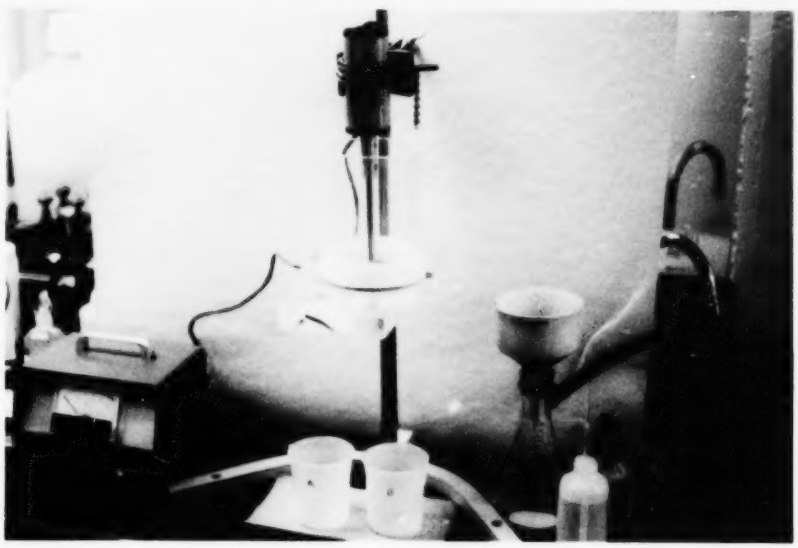


Figure 8. Dynamic Retention/Drainage Jar

The jar consists of a barrel that screws into a round base with a recessed bottom. Two gaskets, a backup perforated plate, and a 76 um hole, 14.5% open area, 0.0508 mm thick screen are positioned between the two. The screen has conical shaped holes with the small opening being placed up when in use. The barrel is 15.24 cm long with a 9.84 cm inside diameter. Three vanes with the dimensions 14.61 cm x 1.27 cm x 0.64 cm are placed at 120^{o} intervals on the perimeter of the jar to equalize turbulence and prevent vortex formation. For a drive unit, a motor generator is used with a servo feedback control

to provide steady speed control from 0 to 3000 revolutions per minute (rpm). The stirrer has a standard 3-bladed, 5.08 cm diameter impeller (40).

This apparatus was manufactured for the purpose of studying the colloidal forces of retention. Since a stirrer is used, no mat forms in the jar during drainage and, therefore, retention attributable to the colloidal forces can be computed from the amount of material in the filtrate from the jar. The apparatus is used widely for screening various retention aids to evaluate their effectiveness. By varying the stirrer speed, retention in the jar can be correlated to machine retention and, therefore, is a very helpful tool in predicting machine response prior to full scale machine trials of a particular retention aid.

Furnish

The furnish used throughout the experimental program is shown in Table 2 below. It is a typical furnish used in the manufacture of high opacity offset paper with a couple of exceptions. Titanium dioxide is usually added at approximately 3 to 5 percent by weight (on fiber); however, to simplify the system, Kaolin clay was used instead. Normally, this filler is added at approximately 10 percent by weight on fiber; however, 20 percent was used to simulate more closely an actual headbox concentration. Pale Pexol, a fortified rosin size, was added for sizing. Reverse sizing (alum-rosin) was used during the experimental program. Analytical grade aluminum sulfate ($Al_2(SO_4)_3 \cdot 16H_2O$) was added as the alum source.

TABLE 2. EXPERIMENTAL FURNISH

COMPONENT	%(Wt.)
Bleached Kraft-Hardwood	48
Bleached Kraft-Softwood	32
Kaolin Clay	20
Rosin Size	0.5
Furnish beaten to 350 CSF in distilled water	
Fines Fraction of Furnish	35

The stock (fiber) was beaten in a hollander beater in distilled water to 350 Canadian Standard Freeness (CSF), dewatered, stored in polyethylene bags at approximately 19 percent moisture, and refrigerated at 4°C. Fresh furnish was made up for each day's activities to 0.5% consistency.

Experimental Design Variables

A maximum of four variables were investigated at any one time during the experimental program. They are shear, alum level, dissolved inorganic level, and dissolved organic level. The variables and quantitative levels for each are shown in Table 3.

Table 3. Independent Variables

Variable	Low	Medium	High
Dissolved Organics* (ppm)	0	550	1100
Dissolved Inorganics** (ppm).	0	94.5	189
Alum (%)	1	2	3
Shear (r.p.m.).	300	600	900

* This represents the actual quantity of dissolved organic concentrate added to each sample. See chemical analyses for characterization of these materials.

**See Table 4 for individual levels of calcium, magnesium, manganese, and iron.

Several levels of shear (turbulence introduced by varying the jar stirrer speed) were used to gather information on how various machines would perform under totally closed conditions. Experimental results showed that the jar retention correlates to the pilot fourdrinier machine retention at 300 rpm. Since this pilot paper machine operates much slower than commercial machines, 300 rpm was used as the low level for this variable. It also affords the opportunity to gather information on how the pilot paper machine will respond to changes in wet end chemistry. The middle and high level rpm settings were chosen as more closely representing actual turbulence levels on commercial machines. This information was taken from industry sources.

The alum levels for the factorial experiments were chosen as one percent above and one percent below the normal industry addition rate of two percent on fiber. These concentrations should indicate the direction in which to move to achieve optimum retention. They were used in several experiments to establish the relationship between alum level and the level of other dissolved substances in the wet end. Several other experiments were conducted where alum was the sole variable and the range of concentrations used covered that expected to be found in totally closed systems in an uncontrolled situation. The maximum concentration was established as 30% alum on fiber. This number was derived from the predicted equilibrium concentration established during the previous totally closed machine run at Miami University in 1977 (1).

Dissolved inorganic levels were also established from the 1977 machine run at Miami University. The maximum concentrations were approximately equal to the predicted equilibrium levels for calcium, magnesium, manganese, and iron. In this experimental program, the levels of dissolved inorganics were treated cumulatively as the various levels of these ions combined. These concentrations are shown in Table 4. The ions were introduced as chloride salts. Analytical grade calcium chloride ($CaCl_2 \cdot 2H_2O$), magnesium chloride ($MgCl_2 \cdot 6H_2O$), manganous

Table 4. Dissolved Inorganic Levels

Inorganic	Low	Medium	High
Iron, as Fe (ppm)	0	7	14
Calcium, as Ca (ppm).	0	65	130
Magnesium, as Mg (ppm).	0	20	40
Manganese, as Mn (ppm).	0	2.5	5

chloride ($MnCl_2 \cdot 4H_2O$), and ferric chloride ($FeCl_3 \cdot 6H_2O$) were used to make up the stock solutions.

The dissolved organic concentrate used as one of the independent variables was derived from the same pulp used as a fiber source for the retention studies. Ten kilograms of bleached kraft pulp (60% hardwood, 40% softwood) was beaten in a pilot scale hollander beater in 225 liters of distilled water to 150 CSF. The pH in the beater was adjusted with HCl to approximately 4.60. The beater used is shown in Figure 9. The contents of the beater were vacuum filtered through a nylon mesh bag and Whatman No. 1 filter paper with the filtrate collected in a stainless steel drum. Figures 10 and 11 show the internal and external layout of the filtering apparatus. This procedure was replicated four times during the study to provide a sufficient quantity of organics. An average of 151.41 liters was recovered through the filtration process. The dissolved material in the filtrate represented, on the average, 81.7 ppm as Total Organic Carbon. Based on the weight of the pulp, approximately 0.18% was solubilized during the beating process.

Concentration of the dissolved organic material in the filtrate was accomplished by reverse osmosis. An Osmonics, Inc., 97E unit, shown in Figure 12, containing three membrane modules operated in series, was used. Each module contained 1.77 square meters of cellulose acetate membrane. The unit operates at a permeate rate of 11.67 cubic centimeters per second (CCS) and at a concentrate rate of 37.32 CCS at an operating pressure of approximately 15 atmospheres. Based on TOC analyses of the raw filtrate and the concentrate, the unit achieved an average recovery of organics of 75.4%.

The concentrate from the unit was lyophilized to dryness. Chemical analyses of the materials were performed by PEDCo Environmental, Inc. and the Institute of Paper Chemistry. Results of the analyses are shown in Table 5. The data shows that carbohydrates represent approximately 23% by weight of the identified organic material. Xylans account for over 80% of this fraction. Uronic acids are the next largest fraction at 2.78% followed by acid insoluble lignin and acid soluble lignin at approximately 2% each. Of the inorganic material identified, calcium represents the largest fraction at 6.3% by weight followed by sodium at 3%. These two elements represent almost 85% of the identified inorganic material in the sample. About 40% of the organic material and 19% of the inorganic were unidentified by the

Figure 9. Pilot Scale Hollander Beater

conventional analyses initially performed. Subsequent analyses using Infrared, Nuclear Magnetic Resonance and Mass Spectroscopy revealed that about 10% of the material exhibited a spectra characteristic of cyclohexylamine. The remaining organic material, about 30% by weight of the sample, exhibited spectra characteristic of organic acids. It is postulated that the material could be calcium oxalate, which would account for the large fraction of calcium in the sample. Calcium oxalate is a common compound found in papermaking systems and is responsible for many deposit problems. In addition, cyclohexylamine is a common compound used as a corrosion inhibitor in power boiler feed water. If the boiler blowdown was being introduced into the process water system, it could account for the relatively high concentration found in the organic concentrate.

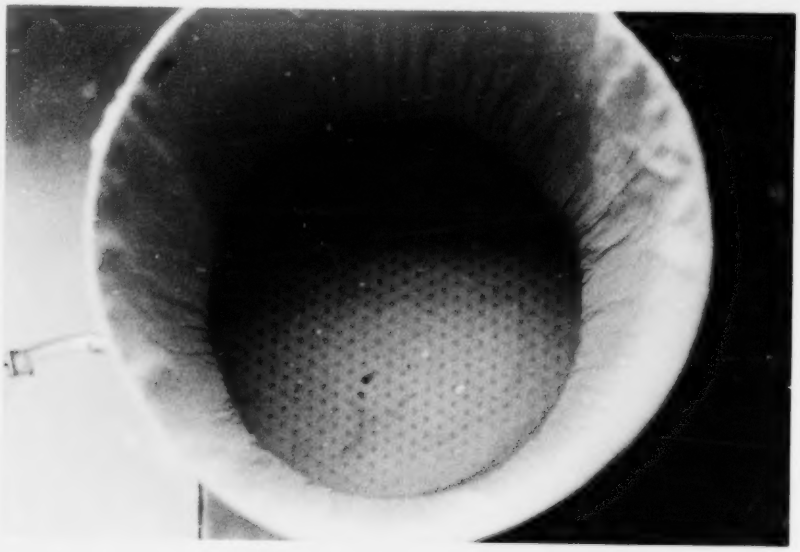


Figure 10. Filtration Apparatus, Top View

Figure 11. Filtration Apparatus, Side View

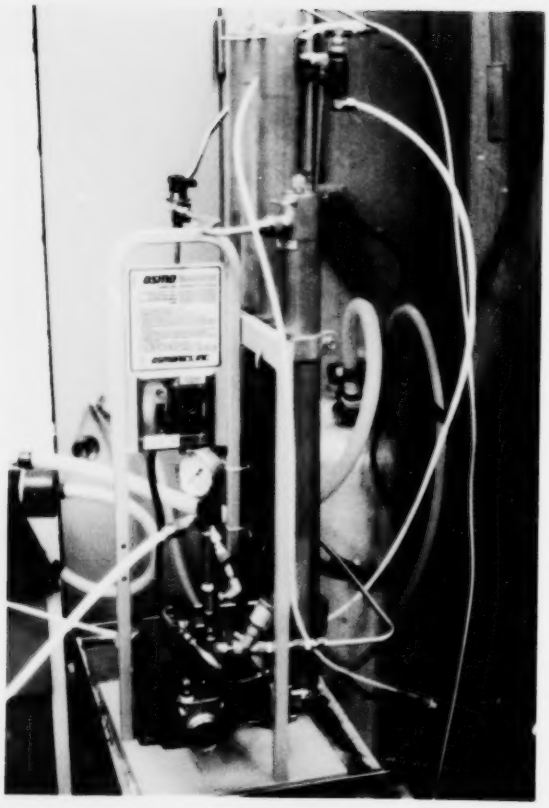


Figure 12. Reverse Osmosis Unit

Experimental Design

Two-level and three-level factorial experiments were conducted using the four independent variables previously discussed. In addition, several one variable experiments were carried out. Statistical analyses of the two-level factorial experiments were performed using Yate's Algorithm. A HP-3000 computer was utilized to perform full quadratic regression analyses on the three-level factorial experiment and on the other one variable experiments. Each experiment will be discussed independently in the Results section.

Experimental Methods

TAPPI Method T261 pm-79 was followed for performing all fines fractionations and retention procedures. The amount of fines in the DRDJ was determined gravemetrically. Whatman No. 42 filter paper or equivalent was used under vacuum to separate the solids in the filtrates. The filter papers were dried in a convection oven at 105°C

Table 5. Organic Concentrate Analysis

Compound	Weight (%)
Acid Insoluble (Klason) Lignin	2.085
Acid Soluble Lignin	1.950
Total Carbohydrate	22.750
Araban	1.150
Xylan	18.400
Mannan	0.650
Galactan	1.000
Glucan	1.550
Uronic Acid	2.780
Oleic Acid	0.003
Linoleic Acid	0.001
Tetrachloroguaiacol	0.033
Chloride	0.192
Sulfate	0.020
Aluminum	0.301
Calcium	6.300
Iron	0.394
Magnesium	0.288
Manganese	0.031
Sodium	3.030
Ash (550°C)	30.100
Unidentified	59.842

overnight, disiccated and weighed on an analytical balance to the nearest 0.0001 gram.

The instrument pictured in Figure 13 is a Model 1133 Zeta Meter manufactured by Zeta-Meter, Incorporated. It was used for the measurement of zeta potential during the experimental program.

Metal and TOC analyses were performed by EPA contractors using EPA accepted analytical procedures.

PHASE II - ALUM TITRATION METHOD INTERFERENCE ANALYSIS

The experimental program designed in Phase I is based on the hypothesis that changes in the uncontrolled variables, with respect to wet end chemistry, i.e., the dissolved inorganic and organic ions, will affect the optimum level of the controlled variable, which is alum. For a wet end optimization strategy to be effective, some fast, efficient means of monitoring the alum level is necessary. Avery (8) discussed the use of an alum titration procedure which can be used to

Figure 13. Zeta Meter

effectively monitor the alum concentration in the system. In addition, a continuous on-line alum monitoring and control system is currently being marketed which is based on the same principle. The technique makes use of a fluoride selective-ion electrode to measure the residual fluoride in solution after the reaction of a 0.1M sodium fluoride titrant with the alum in a whitewater sample from the paper machine. It was hypothesized that any compound in the system besides alum might present the possibility of interfering with the titration either by reacting with the fluoride (a positive interference), or by reacting with the alum and making it inaccessible to the fluoride (a negative interference). Therefore, it was the objective of this phase to determine whether or not the concentrations of dissolved inorganic and organic compounds expected to be found in totally closed systems would interfere with the titration.

Apparatus

Figure 14 shows the basic equipment required for performing the alum titration procedure. It consists of an expanded scale pH meter with two electrodes; one is a fluoride electrode and the other is a standard calomel electrode normally used for pH determinations. All plastic labware is used since fluoride will react with glass. A standard fluoride solution is required for meter calibration as well as a total ionic strength adjustment buffer solution. Stock solutions of the 0.1M sodium fluoride titrant and a pH buffer are required for analyzing samples. The procedure for making up the stock solutions and running the analyses is shown in Appendix B.

Figure 14. Alum Titration Apparatus

Variables: Experimental Design

A series of simple comparison experiments were conducted holding the alum concentration at a low level (100 ppm) and the suspected interfering compounds at high levels. The interfering compounds and their levels are shown as the high levels in Table 3. These interfering compounds were dissolved organics, iron, calcium, magnesium, and manganese. Each experiment was replicated five times.

PHASE III - PILOT SCALE PAPER MACHINE TRIALS

This phase of research was designed to test a wet end optimization strategy based on the monitoring and control of alum concentrations in the system. To complete this task, several trials were performed on a pilot scale fourdrinier paper machine at Miami University.

Equipment

Figure 15 shows the pilot scale fourdrinier machine looking from the wet end toward the dry end. The machine is a stainless steel unit of approximately 7.6 meters in length and is capable of running at speeds of up to 12.2 meters per minute. It is equipped with a straight-through first press, reverse second press, a smoothing press in which the rolls can be changed, dryer sections, six roll machine calendar, and an external slitter and sheeter. Separate control consoles permit push-button regulation of the machine's functions: speed

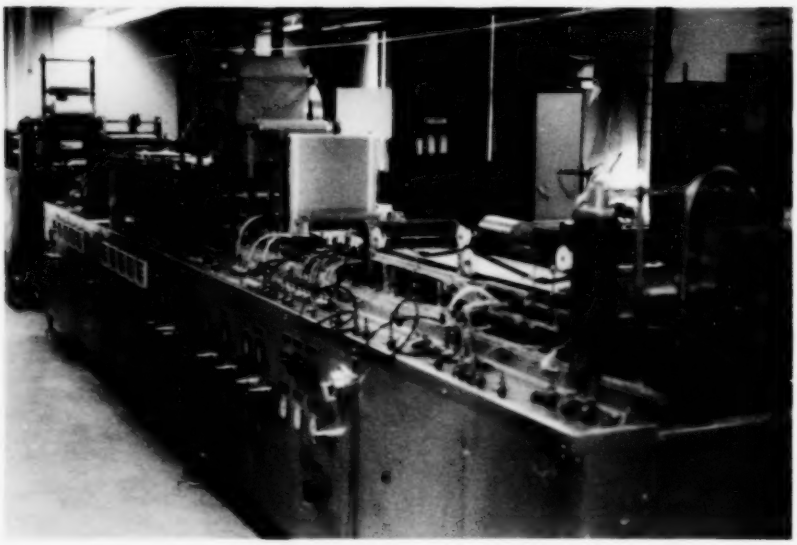


Figure 15. Pilot Scale Fourdrinier Machine

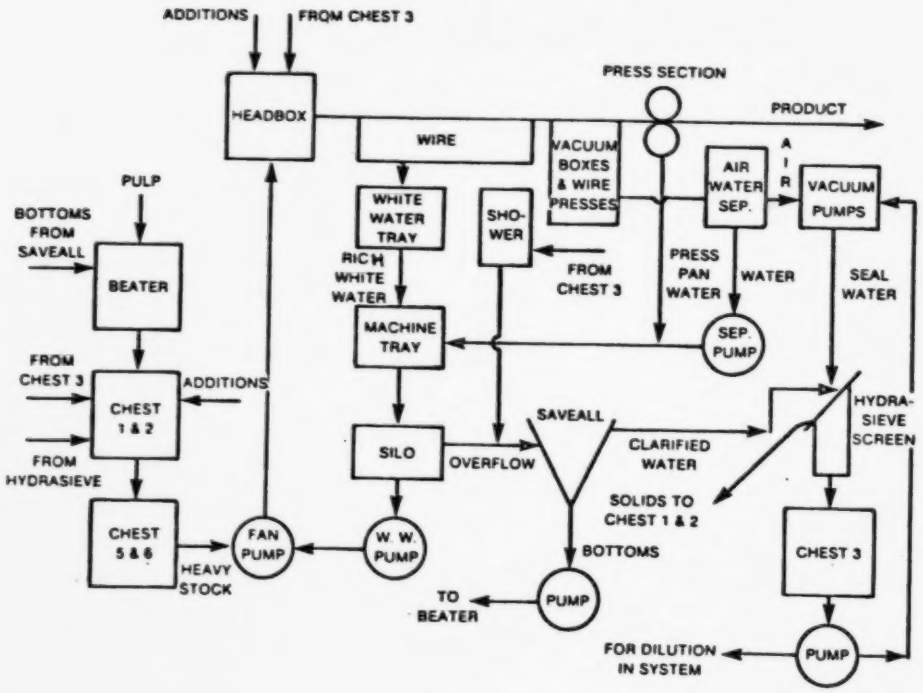


Figure 16. Flow Diagram of Miami University Paper Machine Under Closed Whitewater Conditions. (Ref. 1, Copyright © 1979. Reprinted from TAPPI Vol. 62, No. 12, P. 80, with permission).

of pumps, stock flow, metering of additives, speed of the machine, and rate of vibration of the fourdrinier screen. Stock preparation equipment consists of a stainless steel pulper, two stainless steel beaters and a midget Jordan refiner. The whitewater system can be operated open or closed.

In Figure 16, the white water system of the Miami University machine is illustrated as it exists under closed white water conditions. No white water is discharged when used in this fashion. All water for dilution comes from Chest 3.

Experimental Design

Several machine runs were performed to evaluate a wet end optimization strategy based on the manipulation of alum levels. Samples were taken from the headbox and white water tray to compute the retention of fines and ash. In certain cases, samples of whitewater were also taken and analyzed for TOC and metal ion concentrations. The University of Cincinnati performed these chemical analyses. In addition, occasional paper samples were taken with various quality analyses being performed at Miami University. Each individual machine run will be discussed in the Results and Discussion sections.

SECTION 6

RESULTS

PHASE I - BENCH SCALE RETENTION ANALYSES

Experimentation in Phase I was designed to meet Objective No. 1 - to determine how the alum demand of the system varies according to changes in wet end chemistry. These changes occur as concentration variations of organic and inorganic ions solubilized from raw materials or found in raw water supplies. As a process variable, alum also affects wet end chemistry through changes in addition rates or as a consequence of accumulation in the whitewater system. Therefore, inorganics, organics, and alum were chosen as three independent variables which represent wet end chemistry in its simplest form. Shear was added as a fourth independent variable to gain insight into wet end chemistry relationships which might occur on commercial machines of various speeds.

The first two experiments (Experiments A & B) were conducted to establish basic relationships between the four independent variables. A three level factorial experiment (Experiment C) was conducted to draw a more complete picture of the alum/organic/inorganic relationship at low shear. Two more two level factorials (Experiments D & E) were conducted at the medium and high shear levels to investigate the alum/organic/inorganic relationship under more turbulent conditions. Experiment F was conducted to understand the relationship between high concentrations of alum, such as might be found in a closed system, and retention in a system where no polymer is used. Experiment G was designed to answer the question of why the zeta potential remained at zero over the wide range of alum concentrations used in Experiment F. All of the previously discussed experiments were conducted prior to the first machine trial. Experiment H was conducted after the first machine trial to test the hypothesis that an alum/polymer interaction occurred in 1977 which may have been responsible for the decrease in retention during that machine trial.

Unless otherwise noted, no polymer retention aids were used, the pH was held constant at 4.50 $\pm$ 0.02 units, the sample consistency was approximately 0.5%, and the responses represent the average of duplicate analyses. Each experiment will be individually discussed.

Experiment A - Alum vs. Shear vs. Inorganics

A two level factorial was used to investigate the effects of these variables on fines retention. The run order, levels of the independent variables, and the response with respect to the dependent variables, first pass fines retention (FPFR) and zeta potential (ZP), are shown in Table 6. Statistical analysis of the results was performed using Yate's Algorithm (42) which is shown in Appendix A. Estimated effects are listed in Table 6.

The results show that increasing shear from 300 to 900 rpm had the most dominating effect, decreasing retention an average of approximately 40%. Alum was the next most dominating effect, decreasing retention an average of 11%, while inorganics had the smallest effect, decreasing retention about 9%. In all cases, increasing the level of shear, alum, or inorganics decreased retention.

The zeta potential results show slight colloidal stability in all cases and show that the charge on the particles has reversed due to the addition of the inorganics and alum. Increasing the alum concentration from 2% to 6% actually decreased the zeta potential somewhat.

Table 6. Experiment A - Alum vs. Shear vs. Inorganics

Run	Alum (% on Fiber)	Shear (RPM)	Inorganics (PPM)	FPFR (%)	ZP (mV)
1	2	300	0	78.2	+23
2	6	900	189	16.9	+26
3	2	900	189	17.5	+27
4	6	300	0	52.6	+16
5	2	300	189	54.7	+29
6	6	900	0	14.9	+16
7	2	900	0	20.7	+17
8	6	300	189	41.5	+24

Estimated Effects: Alum (-11.29%), RPM (-39.25%, Inorganics (-8.97%), Alum/RPM (8.16%), Alum/Inorganic (4.39%), RPM/Inorganic (8.36%), Alum/RPM/Inorganic (-1.79%), 95% Confidence Limits $\pm$ 2.42%.

Experiment B - Alum vs. Organics vs. Inorganics

This two level factorial was conducted at the low shear level (300 rpm) to investigate the interaction between the controlled variable alum and the normally uncontrolled variables organics and inorganics. The run order, levels of independent variables, and the responses are shown in Table 7.

Statistical analysis of the results was performed using Yate's Algorithm. The algorithm is shown in Appendix A. Estimated effects are listed at the bottom of Table 7.

The analysis shows that organics had the most dominating effect, decreasing retention on the average of 14%. Increasing the alum concentration from 0% to 2% on fiber decreased retention about 3% on the average. Overall, increasing the inorganic concentration had no effect on retention although there was a significant organic/inorganic interaction. It is somewhat misleading to evaluate results "on the average". It seems that, according to the initial electrokinetic state of the system, retention may increase or decrease with the addition of inorganics. Any change which will change the zeta potential of the system closer to zero generally improves retention; however, the data indicates exceptions to this rule, especially when the organics are added. In all cases, the addition of organics decreased retention even though the zeta potential is closer to the isoelectric point.

Table 7. Experiment B - Alum vs. Organics vs. Inorganics

Run	Alum (% on Fiber)	Organics (PPM)	Inorganics (PPM)	FPFR (%)	ZP (mV)
1	0	0	0	49.1	-20
2	2	1100	189	34.6	- 6
3	0	1100	189	38.3	- 7
4	2	0	0	51.5	+16
5	0	0	189	50.5	+17
6	2	1100	0	31.5	- 6
7	0	1100	0	34.5	-11
8	2	0	189	43.8	+30

Estimated Effects: Alum (-2.76%), Organics (-14.04%), Inorganics (0.12%), Alum/Organic (-0.61%), Alum/Inorganic (-2.45%), Organic/Inorganic (3.33%), Alum/Organic/Inorganic (2.11%), 95% Confidence Limits $\pm$ 2.70%).

Experiment C - Alum vs. Organics vs. Inorganics

This three level factorial experiment was conducted at the low shear level (300 rpm) to further document the relationship between changes in wet end chemistry and retention. The results are shown in Table 8.

Statistical analysis of the data was performed using a full quadratic regression model. This analysis is shown in Appendix A. A review of the t values for the regression coefficients reveals that organics had the most significant effect on retention, with increasing concentrations of organics causing retention to decline. This effect is shown graphically in Figure 17. At 1% alum, and 1100 ppm organics,

Table 8. Experiment C - Alum vs. Organics vs. Inorganics

Run	Alum (% on Fiber)	Organics (PPM)	Inorganics (PPM)	FFPR (%)	ZP (mV)
1	3	0	189	78.5	+34
2	3	550	189	80.6	0
3	1	1100	189	74.9	0
4	2	0	94.5	86.5	+24
5	2	1100	94.5	72.8	0
6	1	1100	94.5	71.3	0
7	2	0	0	81.4	+23
8	1	0	94.5	79.4	+16
9	3	550	94.5	78.0	0
10	2	0	189	79.1	+24
11	3	0	0	84.4	+17
12	2	1100	0	71.3	- 7
13	1	1100	0	61.9	- 8
14	1	550	189	76.8	0
15	3	1100	94.5	72.4	- 5
16	3	550	0	82.3	0
17	1	0	189	78.1	+29
18	3	1100	189	74.5	0
19	3	0	94.5	81.4	+27
20	2	550	0	80.7	- 5
21	1	0	0	85.8	+26
22	2	550	94.5	76.1	0
23	1	550	0	68.8	- 6
24	2	550	189	77.0	0
25	1	550	94.5	75.5	0
26	3	1100	0	79.5	0
27	2	1100	189	81.0	0

Computed T Values: Inorganics (-1.84), Organics (-4.20), Alum (0.68), Inorganics^2 (1.37), Organics^2 (-0.31), Alum^2 (-0.62), Inorganics/Organics (3.97), Inorganics/Alum (0.26), Organics/Alum (3.36), Inorganic/Organic/Alum (-2.74), $T_{0.05,\ 17} = 2.11$

the decrease in retention was approximately 24%. At 2% alum, the effect was much less dramatic, with the decrease being about 6%. At 3% alum, there was no significant decrease in retention.

The effect of inorganics was not significant; however, there was a significant inorganic/organic interaction. This is illustrated in Figure 18. Adding inorganics to a system initially exhibiting a positive zeta potential decreased retention approximately 8%, whereas adding them to a system containing organics and exhibiting a negative zeta potential increased retention 4% to 8% depending on the level of organics.

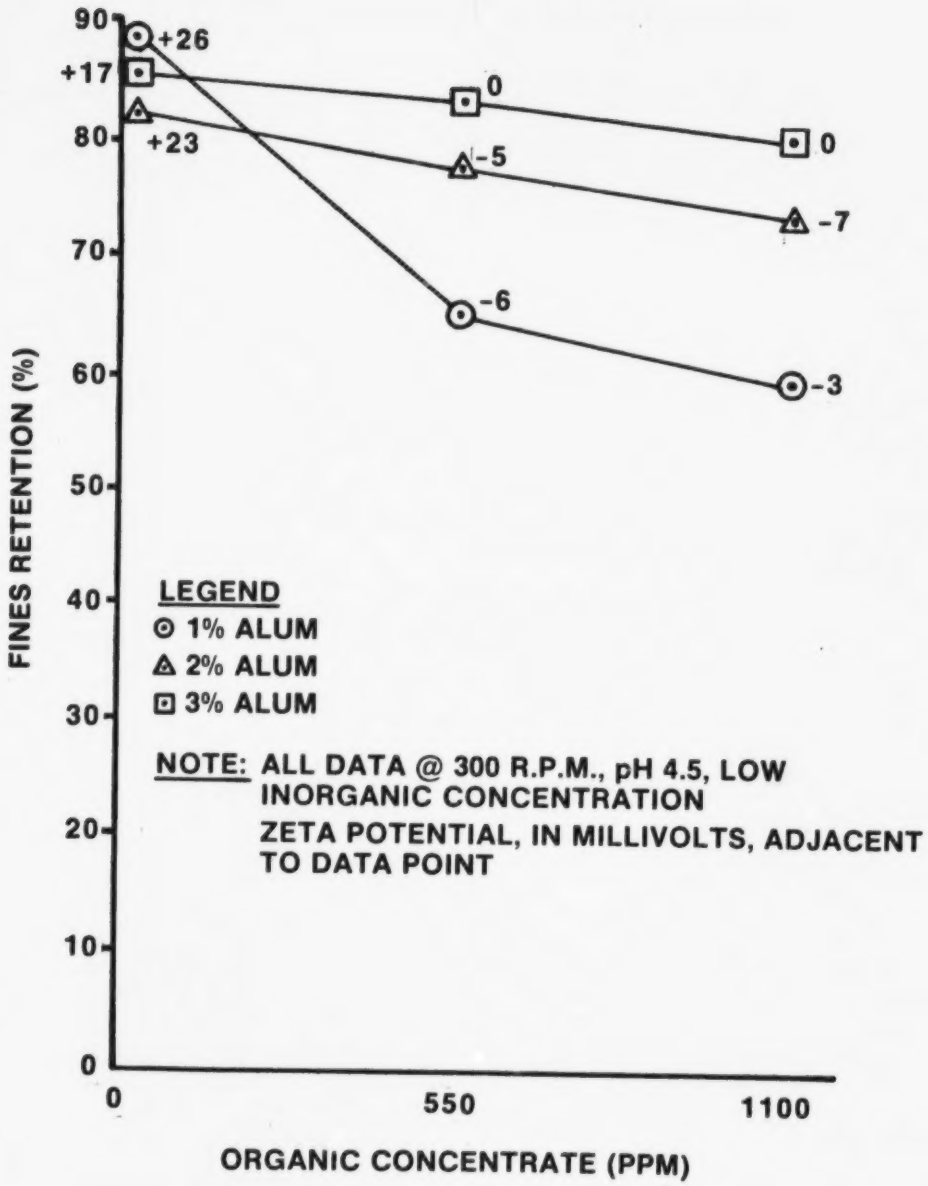


Figure 17. Experiment C - Fines Retention vs. Organics

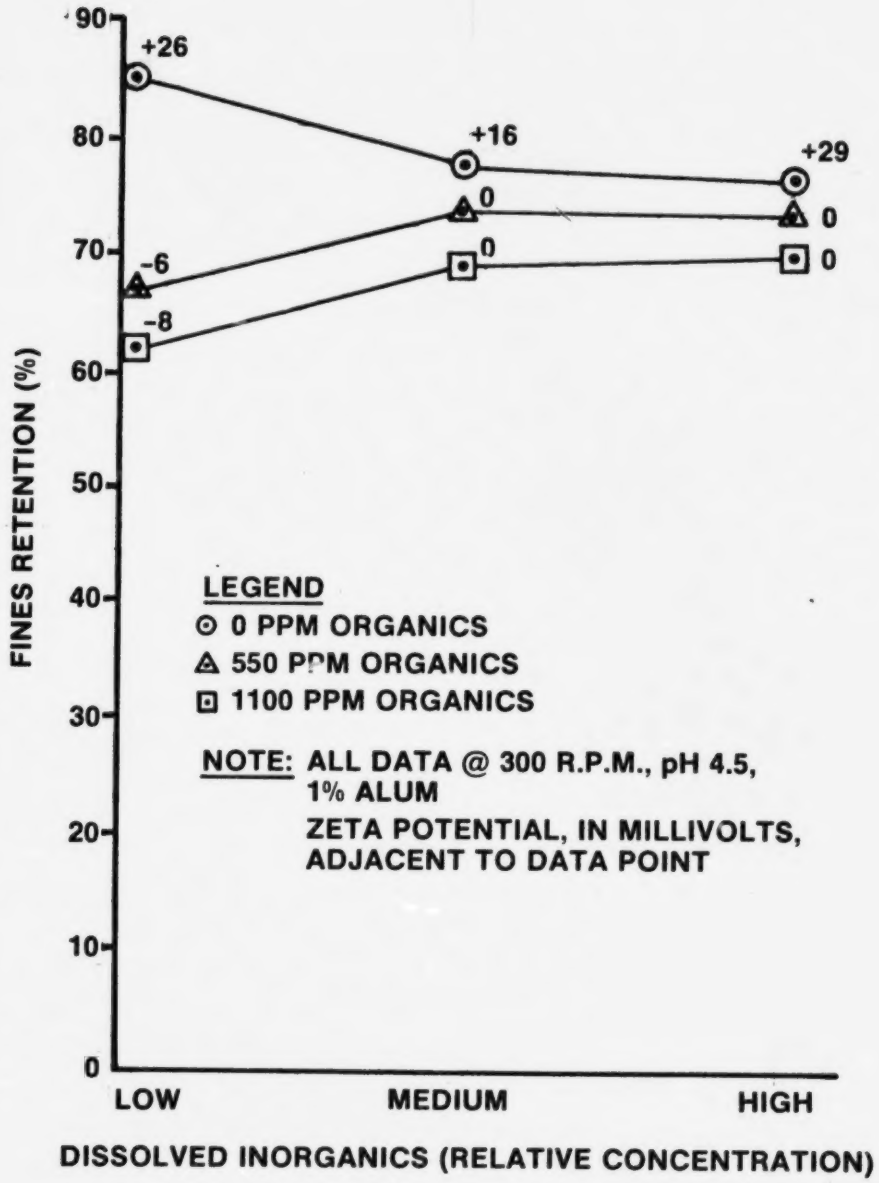


Figure 18. Experiment C - Fines Retention vs. Inorganics

Figure 17 also illustrates the effect of alum on retention. Statistically, the organic/alum interaction was significant. Increasing the alum concentration from 1% to 3% eliminated the negative effect due to organics. It is apparent that the organic material, which is anionic in character, is causing a significant alum demand.

Experiments D&E - Alum vs. Organics vs. Inorganics at Medium and High Shear Levels

Two factorial experiments were conducted, one at the medium shear level (600 RPM) and one at the high shear level (900 RPM), to see if the effects apparent at low shear are also apparent in systems having characteristically higher turbulence. Each two level factorial experiment was individually analyzed using Yate's Algorithm. These statistical analyses are shown in Appendix A. Estimated effects are listed at the bottom of Tables 9 & 10.

Table 9 tabulates the results at the medium shear level (600 RPM). Organics had a negative effect on retention. However, the magnitude of

Table 9. Experiment D - Alum vs. Organics vs. Inorganics (Medium Shear)

Run	Alum (% on Fiber)	Organics (PPM)	Inorganics (PPM)	FPFR (%)	ZP (mV)
1	1	0	0	34.7	+14
2	3	1100	189	30.6	-10
3	1	1100	189	27.7	- 5
4	3	0	0	33.8	+22
5	3	1100	0	28.6	- 5
6	1	0	189	30.2	+23
7	3	0	189	35.8	+25
8	1	1100	0	28.3	- 9

Estimated Effects: Alum (-0.25), Organics (-4.80), Inorganics (1.95), Alum/Organic (0.95), Alum/Inorganic (2.28), Organic/Inorganic (-0.36), Alum/Organic/Inorganic (-0.99), 95% Confidence Limits $\pm$2.68

the effect was less than at the low shear level. At 1100 ppm of organics, the decrease was approximately 7% versus the 24% decrease which was apparent at low shear. Overall, the effect of organics was to decrease retention 4.8%. The effect of inorganics and alum was not significant at the medium shear level. As can be seen, the relative level of retention was much lower at 600 RPM than at 300 RPM, illustrating the negative effect of high turbulence on retention.

Results at the high shear level (900 RPM) are shown in Table 10. Three effects were significant with the alum/organic interaction being the largest. It caused an overall decrease in retention of 3.4%. Varying alum from one to three percent decreased retention an average of 1.9%. There was also an alum/inorganic interaction which caused retention to decrease 1.5%. Overall, retention at 900 rpm was very low, being on the order of 20 to 25 percent.

Table 10. Experiment E - Alum vs. Organics vs. Inorganics (High Shear)

Run	Alum (% on Fiber)	Organics (PPM)	Inorganics (PPM)	FPFR (%)	ZP (mV)
1	3	1100	189	20.3	- 4
2	1	0	189	22.4	+16
3	1	0	0	23.1	- 4
4	3	1100	0	21.2	- 6
5	1	1100	189	26.8	- 8
6	1	1100	0	25.4	-15
7	3	0	189	22.2	+18
8	3	0	0	26.4	+15

Estimated Effects: Alum (-1.90), Organics (-0.09), Inorganics (-1.09), Alum/Organic (-3.44), Alum/Inorganic (-1.50), Organic/Inorganic (1.36), Alum/Organic/Inorganic (0.28), 95% Confidence Limits $\pm$ 1.37

Experiment F - High Alum Concentrations vs. Retention

This experiment was conducted to test the hypothesis that the high concentrations of alum observed during the 1977 closed machine run at Miami University could have caused the decrease in retention which was evident during that run. At the end of that 96 hour run, alum had built up to approximately 15% on fiber based on 0.5% consistency, with the predicted equilibrium of 30% on fiber. Experiment F was conducted at low shear, high organic concentration and low inorganic concentrations. TOC was measured in the jar filtrate as well as first pass ash retention (FPAR). The results are tabulated in Table 11 and graphically illustrated in Figure 19.

Several observations can be made from the results. First, increasing the alum concentration from 0 to 10% significantly increased retention. At concentrations greater than 10%, however, retention decreased somewhat. This trend was evident for both fines retention and ash retention. Second, the TOC in the jar filtrate showed a marked decreasing trend which means the retention of organics continually improved with increasing alum concentrations. This is illustrated in Figure 20. And third, while retention peaked at 10% alum and zero zeta potential, the zeta potential of the particles did not reverse

even up to alum concentrations as high as 30% on fiber. Separate experiments were conducted to investigate this phenomenon.

Table 11. Experiment F - High Alum Concentrations vs. Retention

Run	Alum (% on Fiber)	FPFR (%)	FPAR (%)	ZF (mV)	TOC (PPM)
1	8	87.6	55.5	-10	208
2	10	89.5	76.1	0	199
3	12	85.5	77.1	0	162
4	16	84.1	70.5	0	170
5	20	81.1	66.8	0	159
6	30	76.0	56.9	0	143
7	0	53.5	8.1	-20	-

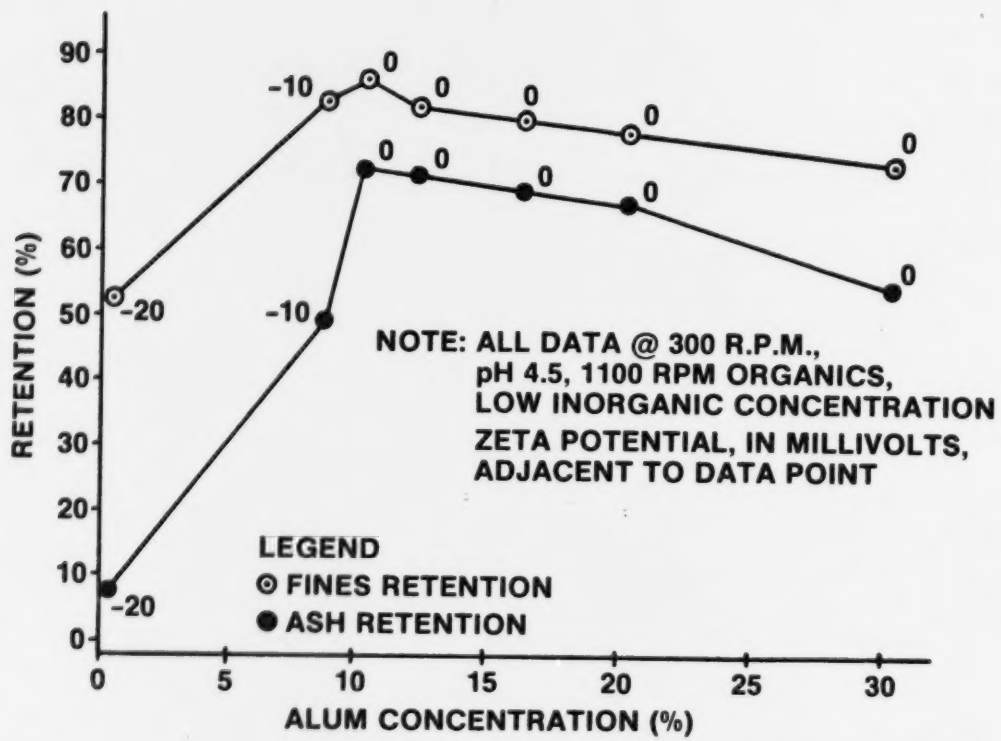

RETENTION (%)
ALUM CONCENTRATION (%)
NOTE: ALL DATA @ 300 R.P.M., pH 4.5, 1100 RPM ORGANICS, LOW INORGANIC CONCENTRATION
ZETA POTENTIAL, IN MILLIVOLTS, ADJACENT TO DATA POINT
LEGEND
FINES RETENTION
ASH RETENTION

Figure 19. Experiment F - Retention vs. Alum

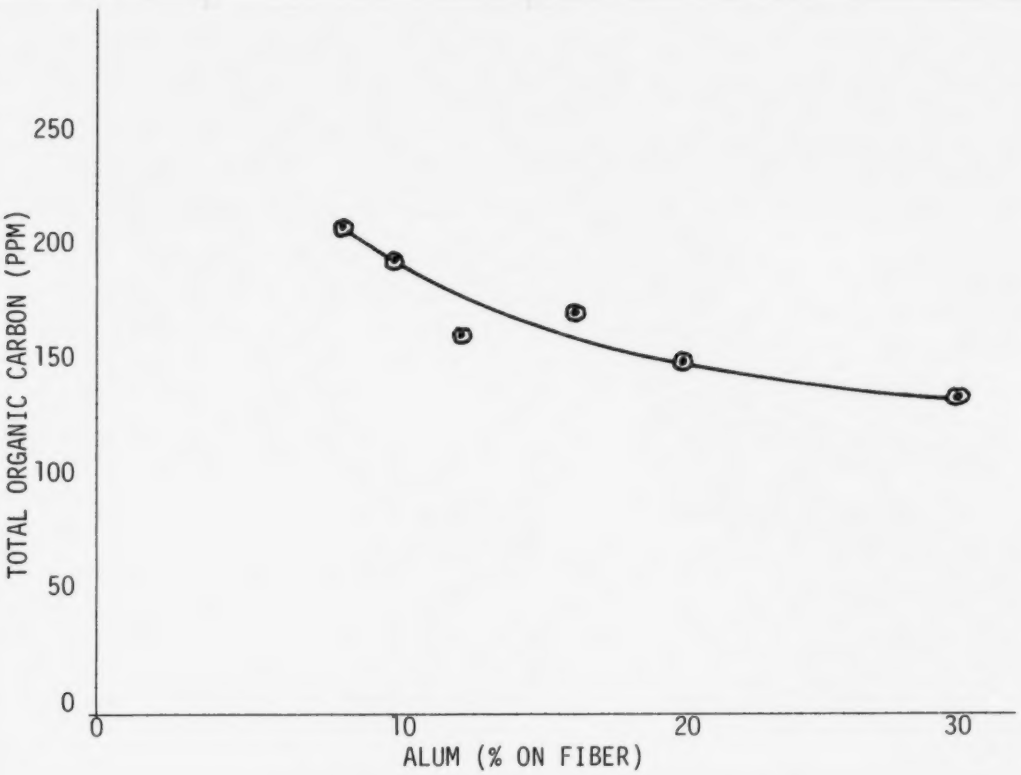


Figure 20. Experiment F - TOC vs. Alum

Experiment G - Organics and Alum vs. Zeta Potential

Various quantities of the organic concentrate were added to the experimental furnish, the fiber was filtered off, and the zeta potential of the fines determined. Figure 21 shows the results of this experiment which was conducted with distilled water. Figure 22 shows the results of the same experiment conducted with tap water.

In both cases, tap water and distilled water, similar curves were obtained using alum and no organic material. The charge on the particles changed from negative to positive at approximately 2% alum. The curve peaked at about +15 mV zeta potential then steadily decreased with further increases in alum concentration. This phenomenon has been previously illustrated in the literature (41) and has been attributed to the formation of aluminum hydroxide and the increasing sulfate ion build up.

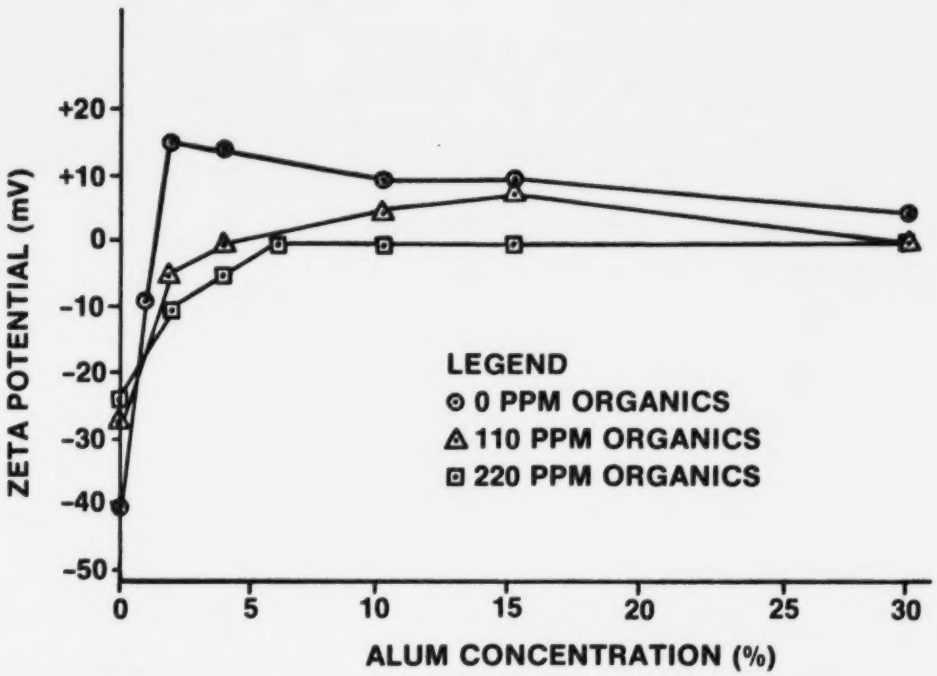


Figure 21. Experiment G - Zeta Potential vs. Alum

Figure 21 also illustrates that the increase in the dissolved organic material in the sample has the effect of suppressing the zeta potential and increasing the alum demand, i.e., the amount of alum required to reach zero zeta potential. The suppression of the zeta potential can also be seen in Figure 22. This phenomenon seems to be characteristic of the organic material. At around 200 ppm of organics, the charge on the particles will not reverse, i.e., will not become positive. It is theorized that a neutrally charged organic polymer is being formed and is coating the particle surface. The effect, coupled with aluminum hydroxide formation and sulfate ion build up, is creating a stable, neutrally charged structure resistant to charge reversal. It is acting in a similar manner in which starch forms a protective colloid.

Two separate sets of data were collected in this experiment. One set used alum as the source of aluminum and the other used aluminum chloride. Clearly, the sulfate ion contributed from the alum acts as an electrokinetic buffer. It complexes with the aluminum ion to form a structure of lower charge, thereby keeping the zeta potential close to the isoelectric point. Chloride is a non-complexing ion; therefore, the aluminum retains its high charge density. Adding additional aluminum chloride will continuously increase the positive zeta potential as illustrated in Figure 22.

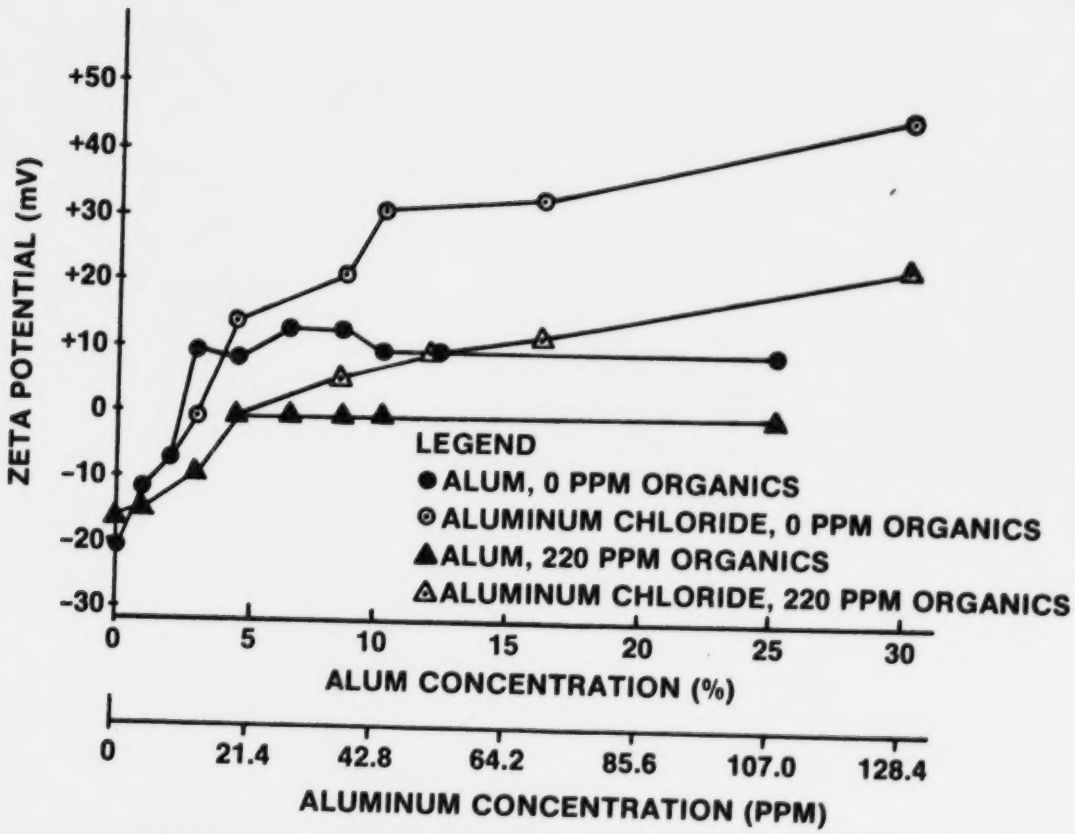


Figure 22. Experiment G - Zeta Potential vs. Aluminum as Alum and Aluminum Chloride

Experiment H - Polymer/Alum Interaction Analysis

Two experiments were conducted to test the hypothesis that the decrease in retention observed during the 1977 closed machine run at Miami University was caused by the effect of high alum concentrations on the effectiveness of the cationic polymer retention aid which was used. These two experiments were conducted with a high molecular weight cationic acrylamide copolymer (Hercules, Inc. Reten 210). The furnish contained 30% ash in the form of filler clay; otherwise, it was the same as the experimental furnish previously used. Two shear levels, 300 and 600 rpm's, were investigated.

Figure 23 shows the results at the low shear level, 300 rpm. The retention curve for the "no polymer" situation shows a characteristic trend with retention increasing sharply and reaching a peak at 86%, with additional alum not resulting in any further increases. Retention levels off at approximately 85%. For the situation where polymer is used at 0.05% on fiber, the results are much different. Retention is

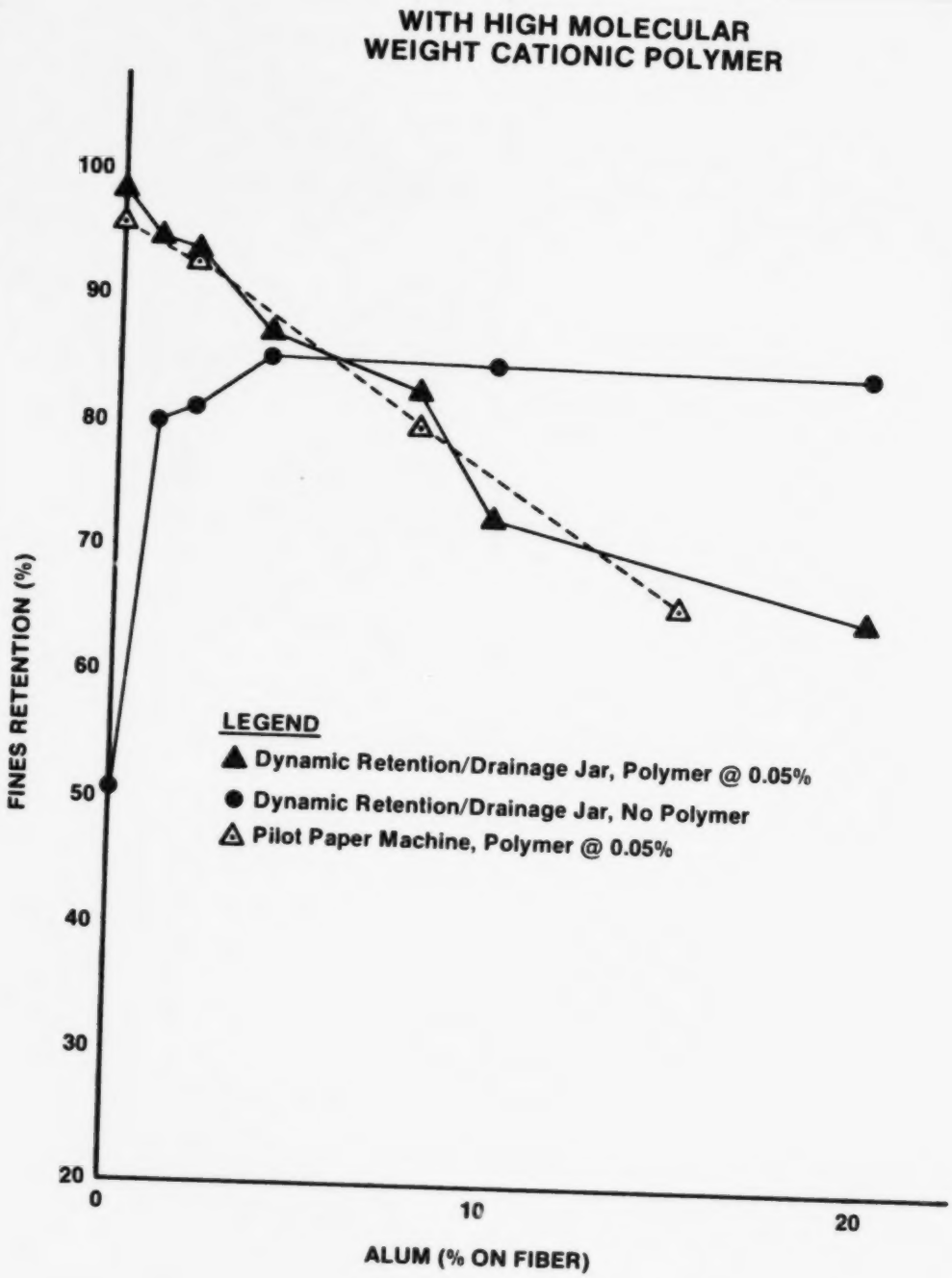


Figure 23. Retention vs. Alum With and Without Cationic Polymer (Low Shear)

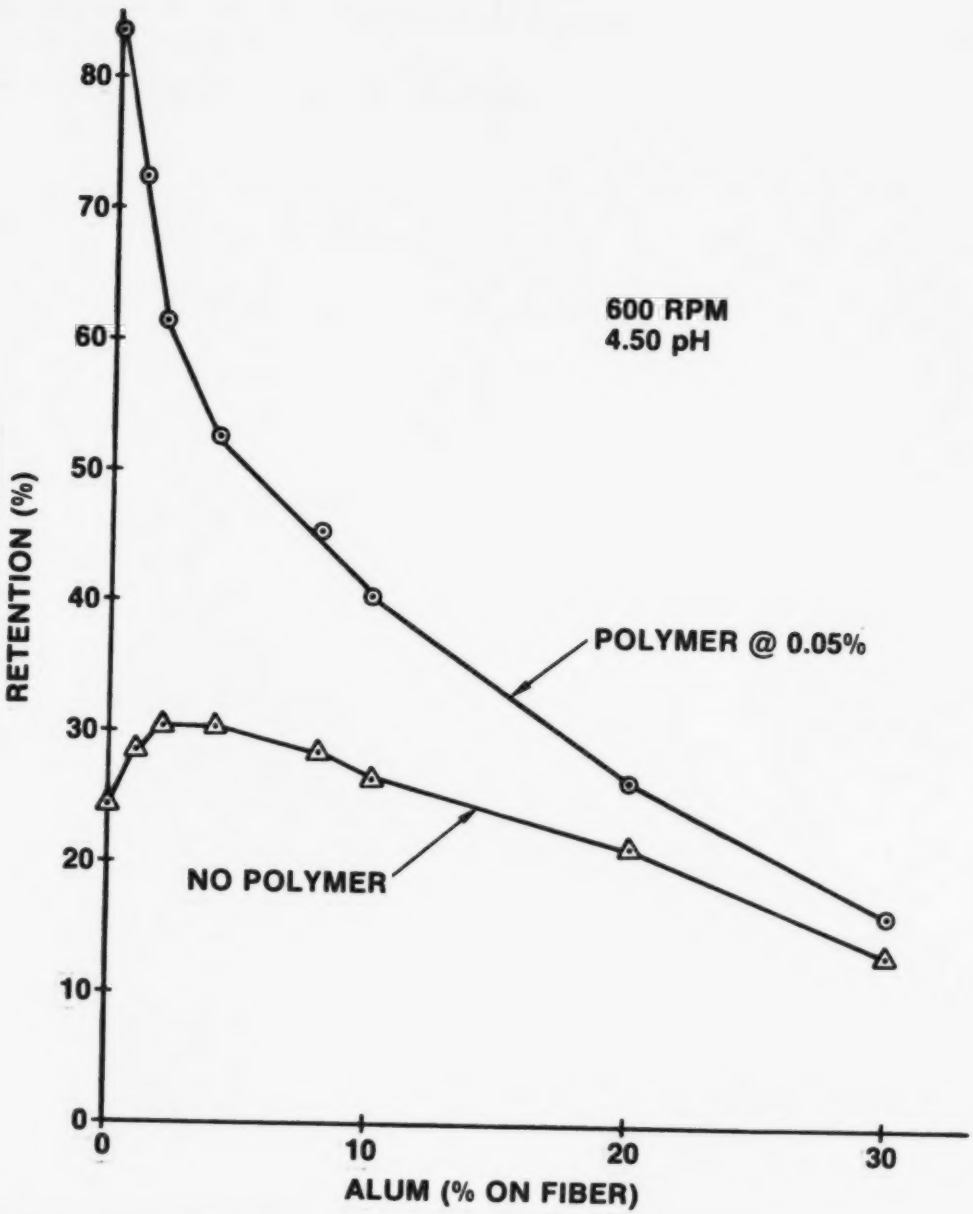


Figure 24. Retention vs. Alum With and Without Cationic Polymer (Medium Shear)

best at 0% alum and continually decreases at higher alum concentrations, from a maximum fines retention of 98% at 0% alum, to a low of 65% at 20% alum. Retention with the polymer is consistently worse than without the polymer at alum concentrations above about 5% on fiber. Alum evidently has a negative effect on the bridging retention mechanism of the polymer.

Figure 24 shows the experimental results at the higher shear level, 600 rpm. The same decreasing trend in retention with the polymer is evident with the magnitude of the effect being much greater. Retention decreased from a maximum of 85% at 0% alum, to a minimum of about 15% at 30% alum. With no polymer retention peaked at 30% at 4% alum, and showed a gradual decreasing trend with increasing alum concentrations.

PHASE II - ALUM TITRATION METHOD INTERFERENCE ANALYSIS

The results of this phase are summarized in Table 12. Average difference is the difference in the outcome of the titration between the sample containing the potential interfering material and the sample containing only alum. The volume of titrant is used to calculate the equivalent amount of alum from a calibration curve. Statistical analysis of the results are contained in Appendix A.

In the case of the organic concentrate and iron, a positive interference of 19 ppm and 5 ppm was observed. If both were present, an interference of 24 ppm as alum may result from their presence in the sample. Therefore, if this sample had been taken from the headbox of a machine operating at 0.5% consistency, the titration would have predicted approximately one half of one percent more alum than was actually present. The interference due to iron was due to the greater affinity to fluoride, having a higher charge density than the other inorganic ions evaluated. The organic concentrate used for the study also contained a substantial quantity of metal ions which could possibly explain the positive interference which it exhibited. Calcium, magnesium, and manganese exhibited no interference at the concentrations expected to be found at equilibrium in a totally closed system.

Table 12. Alum Titration Interferences

Substance (ppm)	Average Difference	
	Volume Titrant (mls)	Alum Equivalent (ppm)
Organic Concentrate (1100)	+0.138	+19
Iron (14)	+0.034	+ 5
Calcium (130)	0	0
Magnesium (40)	0	0
Manganese (5)	0	0

PHASE III - PILOT SCALE PAPER MACHINE TRIALS

It was the goal of Phase III to demonstrate the necessity for, and the mechanics of, a wet end retention control strategy based on the manipulation of alum concentrations in the pilot scale fourdrinier papermaking system at Miami University. To accomplish this goal, several machine trials were performed and are summarized individually below.

Machine Trial No. 1 - 46 Hour Duration

This first trial was conducted to gather baseline data on how paper quality and whitewater chemistry are affected in a totally closed system where furnish components are added at fixed rates. The furnish used was the same as that used during the 1977 machine trial at Miami University, i.e., 55% hardwood kraft, 35% softwood kraft, 7% kaolin clay, 3% titanium dioxide, 0.5% rosin, and 2% alum, with the exception that no dyes or retention aids were used. Reverse sizing was practiced. Headbox samples were taken hourly and analyzed for consistency, fines content, alum, and percent ash. Tray samples were taken hourly and analyzed for consistency, fines content, alum, percent ash, turbidity, specific conductance, and electrophoretic mobility. Headbox and tray samples were also taken at six times equally spaced throughout the trial and analyzed for TOC, dissolved carbohydrates, sulfate, calcium, magnesium, iron, and manganese. Temperature and pH were recorded continuously during the trial. Paper samples were collected hourly and analyzed for basis weight and Hercules sizing. Analyses for caliper, smoothness, brightness, opacity, burst, fold, tensile, tear, and relative stability (% loss of fold) were carried out on samples taken at selected points throughout the trial. Chemical analyses of the headbox and tray samples are summarized in Table 13. Paper properties are summarized in Table 14.

During this first trial, alum was added at 2% on fiber for the first 34 hours. After it was apparent that the retention of fines had not varied dramatically, it was decided that alum addition would be increased incrementally to determine if changes could be induced. In hours 35 to 37, 4% alum was added; for hours 38 to 40, 8% alum; for hours 41 to 44, 16% alum; during hour 45, 32% alum; and during hour 46, 64% alum on fiber was added.

Figure 25 shows the retention data plotted against time, along with the pH, headbox fines, and temperature data. Generally, retention remained very high during the run with fines retention about 80% and ash retention about 70%. pH control was rather erratic covering the range 4.05 to 5.20. Fines concentration in the headbox remained fairly stable at approximately 31%. Temperature in the headbox showed a steadily increasing trend from 20°C at hour 1 to 31°C at hour 46. Figure 26 shows the alum concentration and specific conductance data. Alum concentration generally showed an increasing trend over the first 17 hours followed by a generally decreasing trend over the next 17 hours to hour 34. Specific conductance followed a similar trend.

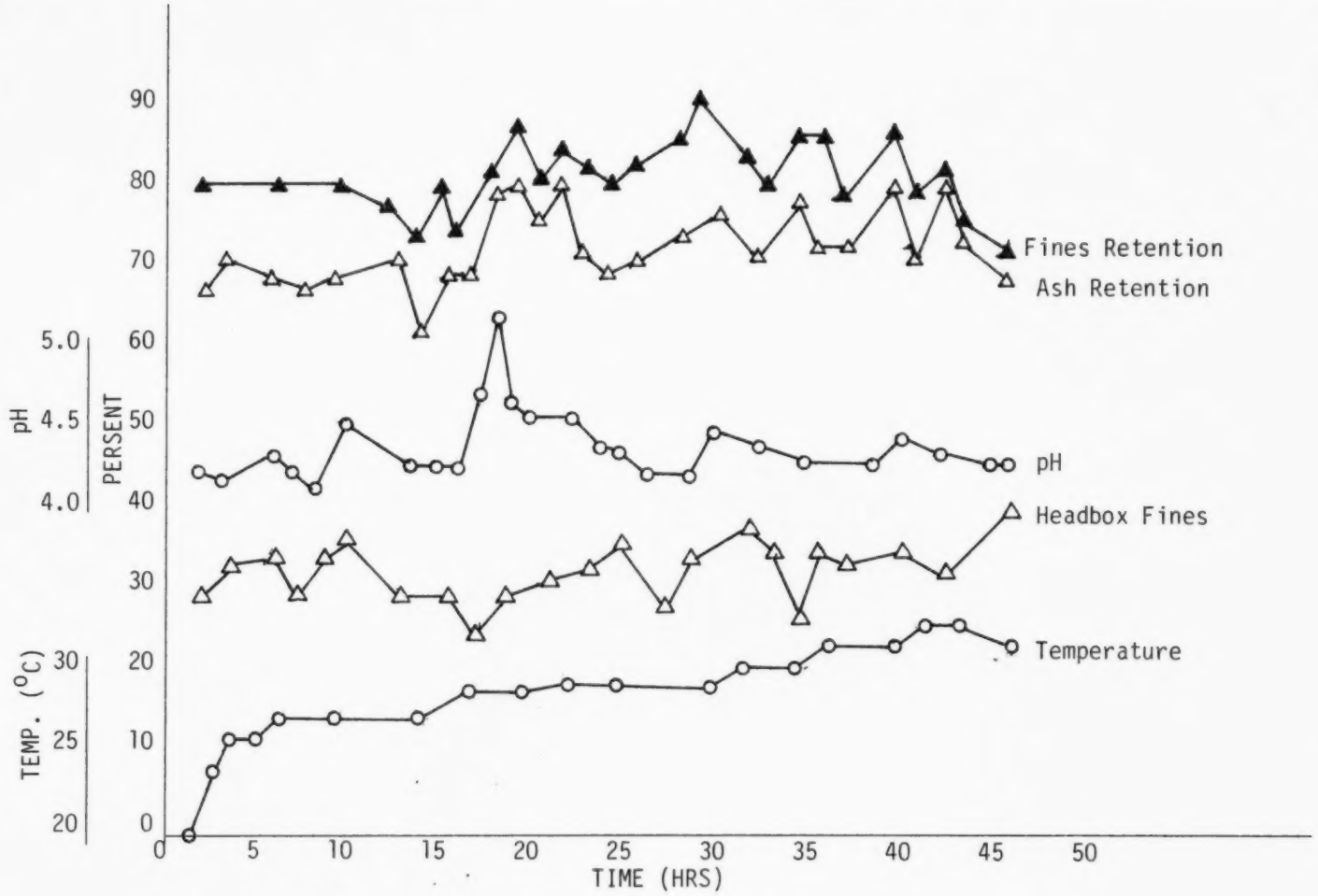


Figure 25. Machine Trial No. 1

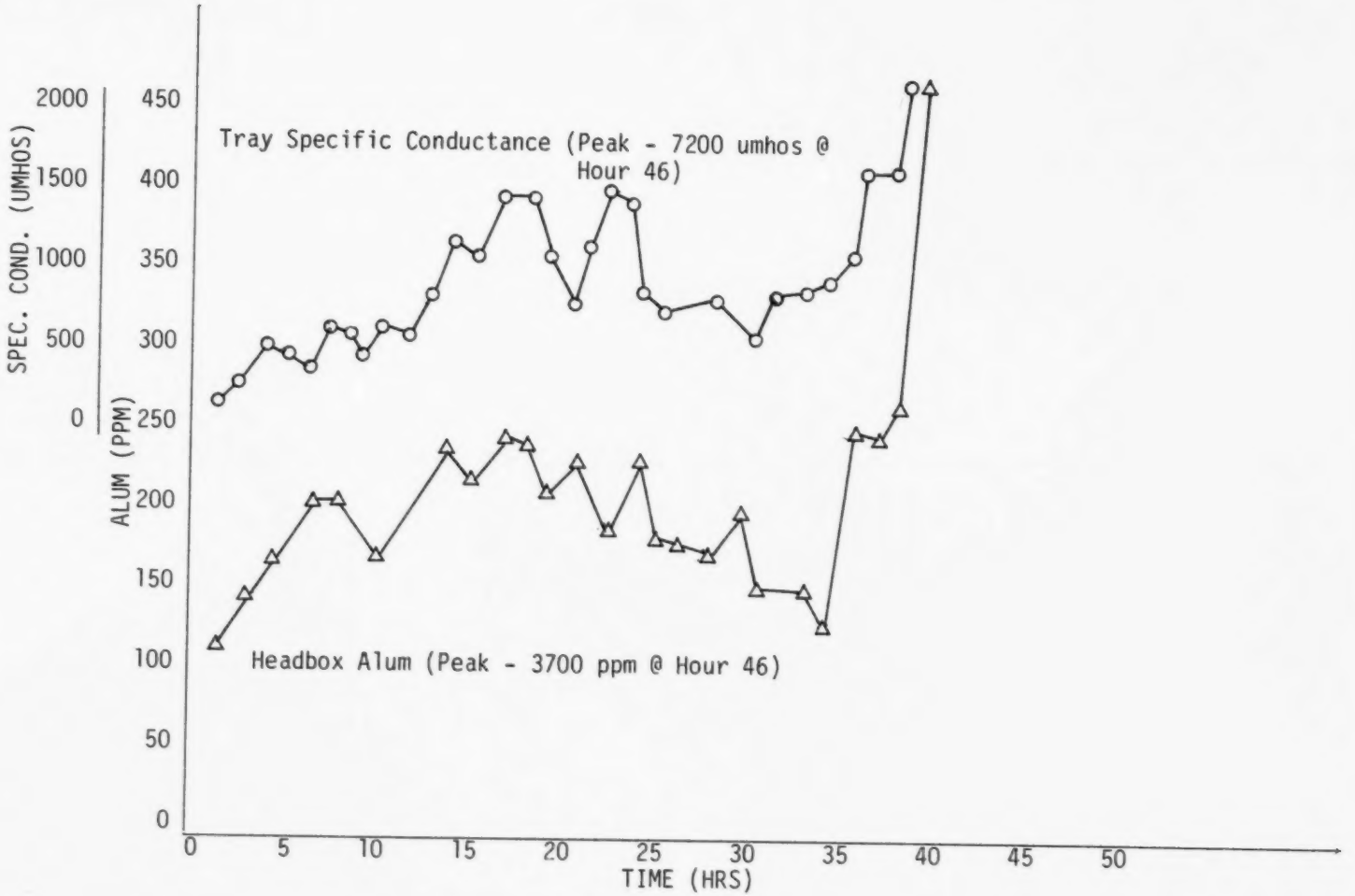


Figure 26. Machine Trial No. 1

TABLE 13. MACHINE TRIAL NO. 1 - CHEMICAL ANALYSES

Parameter	Hour 1	12	24	37	46
Iron (Fe^{3+}, ppm)					
Headbox	0.035	0.420	0.395	0.405	0.740
Tray	0.180	0.190	0.270	0.275	0.360
Manganese (Mn^{2+}, ppm)					
Headbox	0.065	0.200	0.260	0.360	0.300
Tray	0.085	0.180	0.280	0.370	0.380
Magnesium (Mg^{2+}, ppm)					
Headbox	24.9	24.1	23.5	37.4	21.0
Tray	34.8	23.5	26.1	26.6	24.8
Calcium (Ca^{2+}, ppm)					
Headbox	49.4	62.5	57.7	56.2	-
Tray	74.5	56.5	68.0	43.1	29.5
Sulfate ($SO^{=}_4$, ppm)					
Headbox	145.3	496.0	669.5	855.4	2467.8
Tray	209.9	340.1	488.5	690.6	2812.6
TOC (ppm)					
Headbox	10.94	16.36	25.20	26.96	25.91
Tray	10.94	16.49	16.09	28.35	23.81
Glucose (ug/ml)					
Headbox	38.75	34.10	97.15	57.80	57.30
Tray	22.00	31.45	60.65	59.40	67.30
Starch (ug/ml)					
Headbox	34.88	30.69	87.43	52.02	46.17
Tray	19.80	28.30	54.80	53.46	60.57

The results of the chemical analyses showed that retention was not adversely affected by the increasing temperature, alum, iron, manganese, calcium, magnesium, or sulfate concentrations in the system. Electrophoretic mobility measurements indicated colloidal particle instability, therefore making conditions right for optimum coagulation. The addition of excessive amounts of alum did not significantly change the electrophoretic mobility and, therefore, would not be expected to change retention significantly. This is exactly what happened. This effect on electrophoretic mobility was also confirmed in earlier bench top studies. The small effects on retention, which were evident, seemed to relate to the changes in pH. Increasing the pH tended to result in increases in fines and ash retention. This was probably due to the precipitation of

TABLE 13. MACHINE TRIAL NO. 1 - CHEMICAL ANALYSES

Hour	HBC (%)	HBF (%)	TRC (%)	TRF (%)	FPFR (%)	FPAR (%)	TREM (%)	TRTB (FTu)
1	0.377	38.5	0.014	100	----	----	-0.52	1150
2	0.534	28.8	0.035	80.8	79.5	65	+0.21	1260
3	0.558	31.3	0.040	77.0	79.4	70	+0.26	1400
4	0.856	21.2	0.049	89.7	----	----	+0.21	1660
5	0.904	31.2	0.037	77.1	----	----	+0.35	1800
6	0.540	32.6	0.041	73.6	79.1	68	+0.48	920
7	0.549	28.8	0.036	85.2	79.5	67	-0.40	880
8	0.534	32.1	0.039	90.1	79.6	65	-0.49	860
9	0.365	----	0.013	63.2	----	----	+0.39	820
10	0.917	34.9	0.042	79.7	79.1	66	+0.41	1040
11	0.527	35.4	0.013	100.0	----	----	-0.34	960
12	0.512	34.6	0.014	100.0	----	----	-0.46	900
13	0.518	27.0	0.013	100.0	----	----	-0.51	920
14	0.510	28.5	0.036	95.2	77.7	69	-0.75	980
15	0.530	30.0	0.049	83.5	72.3	60	-0.85	1000
16	0.525	28.8	0.034	90.8	79.8	67	-0.47	900
17	0.491	----	0.032	83.7	----	67	-0.72	860
18	0.546	28.6	0.036	91.4	79.3	79	-0.48	650
19	0.549	31.8	0.026	89.5	86.6	80	-0.39	650
20	0.523	27.7	0.031	83.5	80.8	75	-0.70	760
21	0.560	30.0	0.030	93.7	83.9	81	-0.61	720
22	0.530	30.4	0.033	97.7	81.6	71	-0.68	700
23	0.563	31.1	0.039	92.5	80.0	68	-0.85	960
24	0.521	33.0	0.033	93.2	----	----	-0.35	950
25	0.547	32.3	0.035	86.3	82.2	70	-0.50	900
26	0.410	----	0.019	100.0	----	63	-0.33	940
27	0.524	26.1	0.032	85.3	79.0	73	-0.36	860
28	0.582	32.4	0.027	98.1	87.1	72	-0.41	960
29	0.476	32.4	0.018	83.7	89.5	----	-0.40	840
30	0.479	35.8	0.012	100.0	----	----	-0.50	840
31	0.508	35.8	0.028	100.0	86.2	76	-0.48	800
32	0.546	33.0	0.033	85.2	83.5	71	-0.44	800
33	0.546	33.2	0.037	84.0	81.7	72	-0.52	920
34	0.519	23.8	0.028	96.0	79.7	72	-0.46	780
35	0.538	33.4	0.031	99.4	84.5	77	-1.16	840
36	0.526	30.4	0.028	98.4	84.3	72	0	760
37	0.544	31.8	0.041	87.6	78.7	72	0	620
38	0.538	31.4	0.039	85.1	79.3	77	0	780
39	0.553	32.9	0.027	100.0	86.2	81	0	740
40	0.545	33.5	0.038	100.0	81.3	69	0	860
41	0.563	33.3	0.032	100.0	84.7	83	0	860
42	0.545	30.9	0.038	92.8	79.7	77	0	960
43	0.552	31.1	0.037	88.5	80.6	----	0	980
44	0.590	28.9	0.039	84.1	79.5	79	0	980
45	0.564	22.1	0.046	92.1	----	74	0	1220
46	0.635	39.5	0.075	100.0	73.2	68	0	1900

TABLE 13. MACHINE TRIAL NO. 1 - CHEMICAL ANALYSES

Hour	TRSC (umhos)	HBT (°C)	HBAL (PPM)	TRAL (PPM)	SOAL (PPM)	SAAL (PPM)	SCAL (PPM)	HBpH
1	174	20	111.5	68.6	74.0	29.3	-----	4.30
2	290	23	144.6	107.3	98.9	58.7	29.3	4.20
3	495	25	159.0	128.7	124.6	79.4	-----	4.15
4	471	25	260.5	201.6	203.1	114.7	70.8	4.15
5	430	25	343.6	259.5	252.6	107.3	-----	4.15
6	345	26	202.8	247.0	141.2	132.8	104.5	4.20
7	555	26	203.2	176.9	173.2	132.2	-----	4.15
8	540	26	219.9	193.5	183.3	115.2	110.1	4.05
9	444	26	152.0	94.4	91.3	87.8	-----	4.55
10	571	26	160.5	137.1	140.0	99.1	-----	4.43
11	555	26	190.6	155.4	140.7	109.3	75.8	4.42
12	833	26	152.8	124.1	105.7	92.1	-----	4.35
13	1110	26	217.8	139.5	142.8	91.5	-----	4.20
14	1098	26	233.2	145.7	121.1	103.2	-----	4.15
15	1332	26	206.3	158.3	154.2	114.6	122.8	4.15
16	1332	26	243.4	170.0	175.0	128.1	-----	4.15
17	1060	27	240.2	145.1	157.2	113.5	-----	4.70
18	821	28	206.1	98.7	84.0	100.3	-----	5.20
19	848	27	220.5	91.5	103.1	78.7	176.4	4.60
20	1141	28	227.2	103.0	91.5	60.4	-----	4.50
21	1382	28	217.9	102.1	84.3	64.2	-----	4.50
22	1369	28	187.8	78.5	70.3	60.3	155.3	4.50
23	1220	28	225.9	104.0	103.6	97.7	-----	4.40
24	768	28	180.6	96.4	101.2	81.7	-----	4.30
25	628	28	176.1	98.4	107.4	87.5	-----	4.28
26	691	28	184.8	107.3	101.1	91.6	-----	4.25
27	648	28	171.2	104.8	113.0	94.9	-----	4.22
28	768	28	-----	118.9	118.4	96.6	-----	4.22
29	648	28	191.0	113.0	117.3	109.8	-----	4.20
30	532	28	155.7	107.2	86.7	87.8	127.0	4.50
31	740	28	148.2	80.7	77.7	64.9	-----	4.45
32	704	29	154.5	74.3	69.3	68.9	101.6	4.35
33	782	29	155.7	76.4	81.4	68.7	-----	4.38
34	844	29	134.9	66.8	64.3	59.1	-----	4.35
35	1055	29	244.3	112.2	103.0	85.4	92.4	4.25
36	1682	31	235.4	106.5	124.0	71.8	-----	4.25
37	1682	31	264.8	102.0	120.6	95.7	-----	4.25
38	1987	31	454.7	120.5	148.4	113.6	-----	4.25
39	2082	31	468.8	150.2	146.6	91.3	-----	4.25
40	3122	31	547.1	163.5	153.7	142.9	-----	4.50
41	3706	32	893.9	161.0	176.3	130.7	169.9	4.30
42	3803	32	989.0	188.3	190.8	150.3	-----	4.40
43	4276	32	1031.8	188.1	162.5	165.6	-----	4.37
44	4411	32	1016.9	177.1	154.9	117.5	-----	4.30
45	5465	31	1270.3	332.6	259.2	240.9	-----	4.30
46	7286	31	3689.6	1232.2	843.1	705.4	-----	4.30

TABLE 14. MACHINE TRIAL NO. 1 - PAPER PROPERTIES

Property	Hour					
	3	14	21	30	37	43
Basis Weight (g/m^2)	103.4	100.0	99.6	94.0	100.0	103.4
Caliper (mm)	0.170	0.166	0.172	0.161	0.169	0.179
Sheffield Smoothness (SFu)						
Wire Side	231	236	248	251	254	258
Felt Side	255	256	269	277	265	265
Sheffield Porosity (SFu)						
Wire Side	61.4	77.4	78.5	89.8	86.3	87.9
Felt Side	64.6	77.4	78.8	86.6	83.1	86.9
Brightness, GE(%)	84.6	85.5	84.5	84.6	84.9	85.4
Opacity (%)	94.5	93.9	94.7	93.7	94.0	94.4
Burst (KPa)	120.0	101.4	105.5	80.7	94.5	80.7
Burst Index ($KPam^2/g$)	1.16	1.01	1.06	0.86	0.94	0.78
Fold (No. double folds)						
MD	5.0	5.0	5.2	4.6	5.0	4.8
CD	3.0	3.0	2.8	2.8	3.0	2.2
Tensile (Kg)						
MD	6.02	5.36	5.26	4.72	5.15	4.95
CD	2.74	2.53	2.70	2.31	2.69	2.47
Elongation (%)						
MD	2.01	2.00	2.07	1.54	1.68	1.50
CD	3.51	2.54	2.67	2.07	2.57	2.27
Tensile Index (Nm/g)						
MD	38.06	35.04	34.53	32.83	33.67	31.30
CD	17.32	16.54	17.72	15.10	17.59	15.64
Tear (g)						
MD	66.9	53.6	60.0	59.2	54.1	52.0
CD	55.4	66.1	66.1	62.9	59.3	50.0
Tear Index						
MD	62.2	51.5	57.9	60.6	54.0	48.4
CD	51.5	63.6	63.9	64.4	61.7	48.1
Relative Stability (% loss of fold)	52.7	----	----	----	75.5	60.0
Hercules Sizing (Seconds)	155.3	220.0	214.0	----	281.5	152

aluminum hydroxide which would tend to increase retention through entrapment of fine solids. The fact that alum concentrations decreased during hours 15 through 34 was probably due to the sharp increase in pH. Caustic addition was initiated during hour 17 causing the precipitation of aluminum hydroxide at dead spots in the system. At the completion of the run, heavy deposits were found in the overflow chest from the saveall and in the hydrosieve sump. Regardless of the loss of alum in the system, adding excessive amounts to the chest did not adversely affect retention.

Machine Trial No. 2 - 4 Hour Duration

During Machine Trial No. 1, retention did not decrease as it had during the 1977 closed machine run at Miami University. It was hypothesized that this was the result of either the higher basis weight which was used (26 lb./ream vs. 22 lb/ream) or the lack of a high molecular weight cationic polymer in the furnish. This second trial's purpose was to test the hypothesis that the higher basis weight caused the relatively high and stable retention levels which existed in Trial No. 1.

Figure 27 shows a plot of alum concentration versus retention at four different basis weights. Generally, retention increased with increasing basis weight. Going from a 17 lb. sheet to a 26 lb. sheet, retention increased about 10%. Again, retention did not decrease greatly with increasing amounts of alum up to 30% on fiber. The decrease was on the order of 3%; however, in one case, the 20 lb. sheet, retention increased about 3% between 10% and 30% alum on fiber.

Machine Trial No. 3 - 4 Hour Duration

This experiment tested the hypothesis that the use of a high molecular weight cationic polymer caused the decrease in retention observed in the 1977 machine run at Miami University. Therefore, not using a polymer in Machine Trials Nos. 1 and 2 may have caused the stable retention levels which existed.

Reten 210, a high molecular weight cationic polymer manufactured by Hercules, Inc., was used for this machine trial at an addition rate of 0.05% on solids. The furnish used was a modified version of that used in Machine Trials 1 and 2. 30% ash (21% clay, 9% TiO_2) was used to more realistically represent actual closed system concentrations of this material. Alum was added at varying concentrations in the machine chest whereas retention aid and pH control (at 4.50) occurred in the headbox. Figure 28 shows the results of the machine trial alongside other data collected on the same furnish using the dynamic retention drainage jar.

The results show that there is a definite alum-polymer interaction such that retention steadily decreases with increasing alum concentration. Dynamic retention/drainage jar results show the same trend as the machine generated results. Retention fell approximately 30% from a high of 96% at 0% alum to 66% at 15% alum during the machine trial. Retention fell approximately 33% from a high of 98% at 0% alum to a low of 65% at 20% alum in the dynamic retention/drainage jar. The figure also shows the general

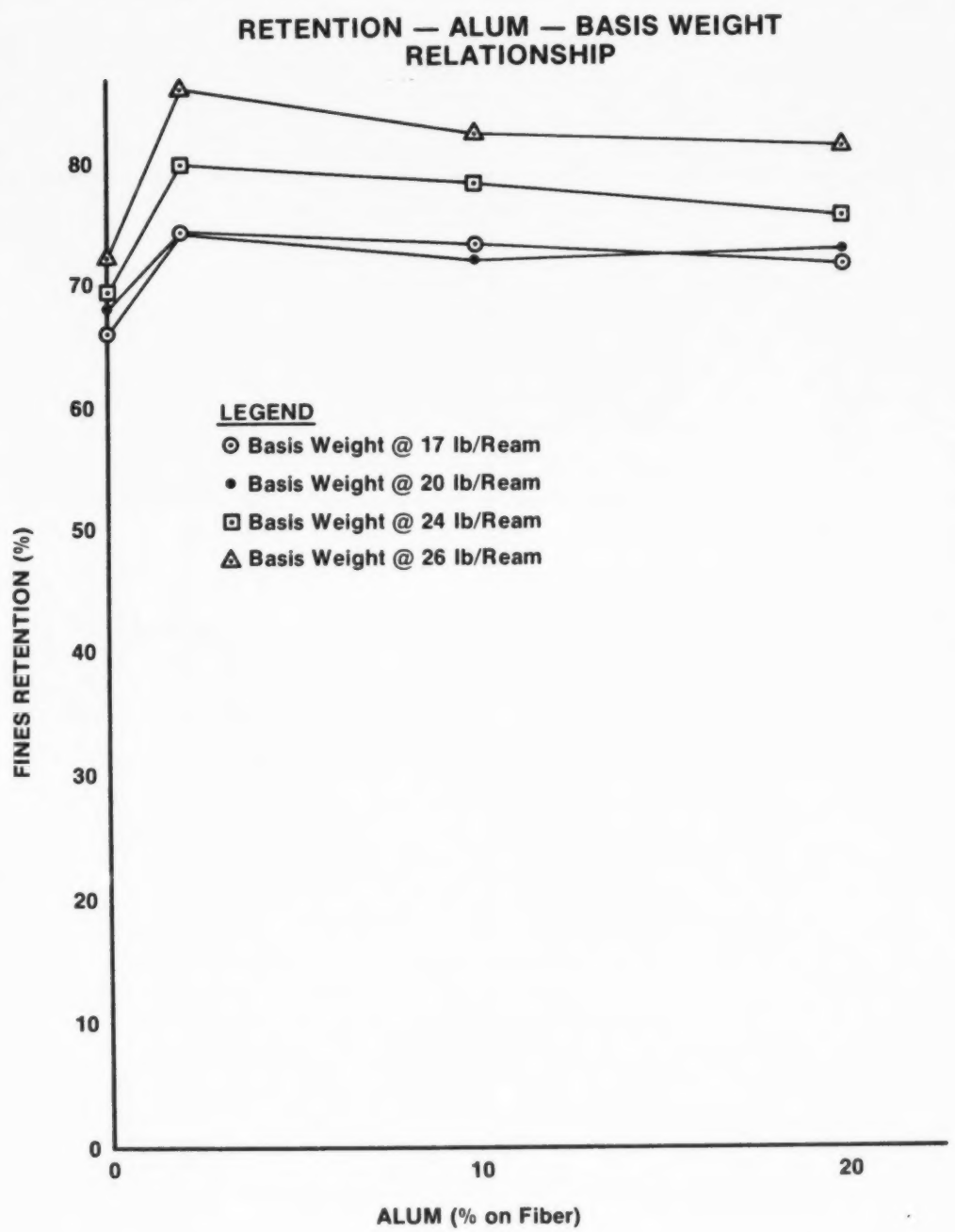


Figure 27. 4 Hour Machine Trial - Effect of Basis Weight on Retention

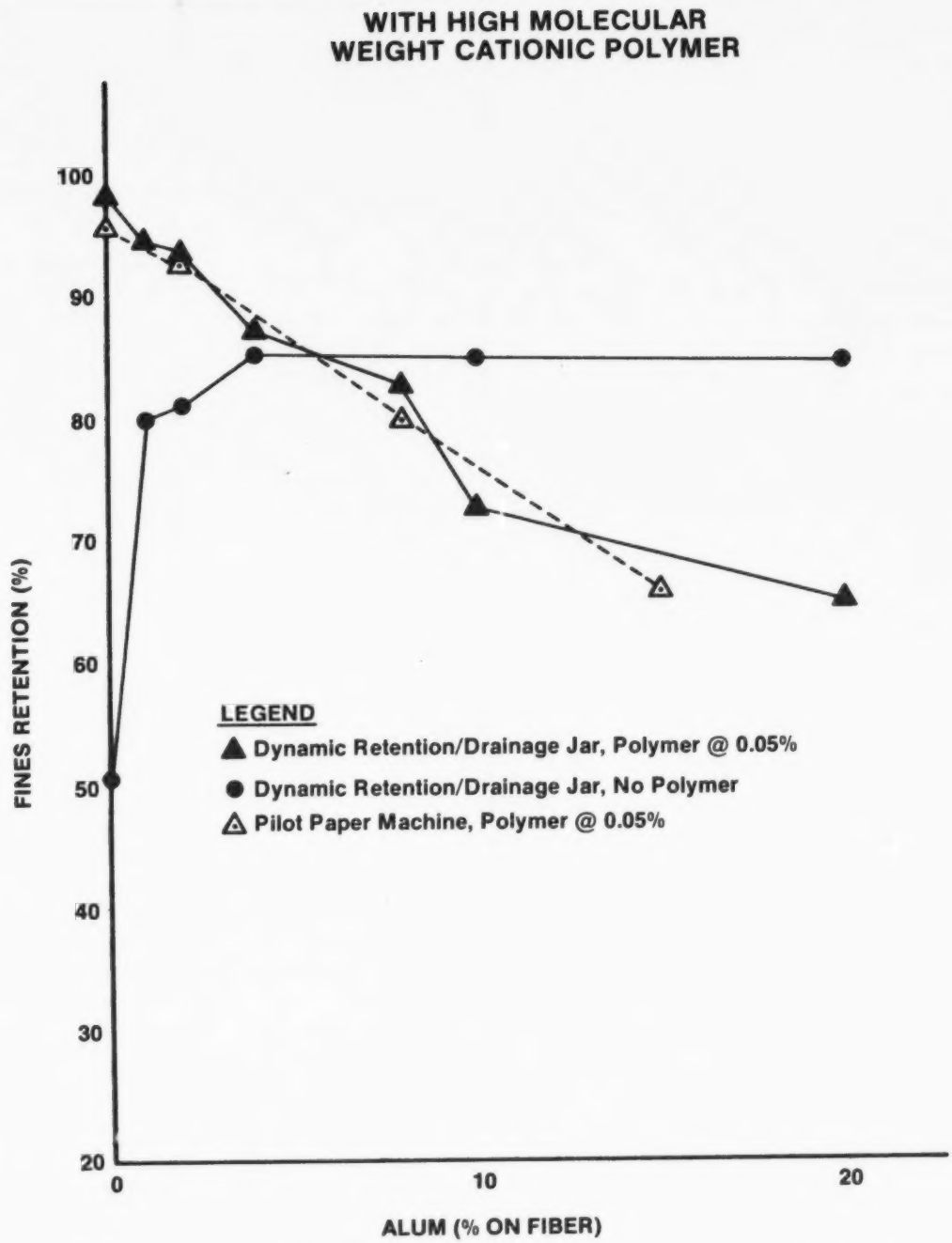


Figure 28. 4 Hour Machine Trial - Effect of Alum on Cationic Polymer

relationship when no polymer is used. Retention increased initially to reach a peak at 85%, at an alum concentration of 4% on fiber. Retention levels remain constant at higher alum concentrations of up to 20% on fiber. This general relationship was also observed in Machine Trial No. 2. It is also observed that at alum concentrations above approximately 6% on fiber there is no added benefit from using the cationic polymer. The more alum which is added, or which builds up in the system, will cause a continued decrease in retention below the level in the system when no polymer at all is used. These results illustrate why alum control is absolutely essential in a system where cationic polymers are being used for retention control.

SECTION 7

DISCUSSION

PHASES I & III - RETENTION ANALYSES

The results presented in Section 6 can be summarized by discussion of the effects of each of the variables investigated, i.e., shear, alum, organics, inorganics, polymer, and basis weight, on retention.

Effect of Shear

In all cases, during this research project, increasing the amount of shear or turbulence decreased retention. This effect was readily apparent during the bench scale retention studies in Phase I. Increasing the turbulence by adjusting the stirrer speed in the dynamic retention/drainage jar from 300 to 900 rpm reduced the level of ash retention below the recommended minimum level of 25% as predicted from the 1977 machine run at Miami University. In this study, when alum was being used as the only retention aid, it became evident that, for medium and high shear commercial machines, some more powerful retention aid, such as a synthetic organic retention aid, would be required.

Where alum is being used as the retention aid, the general relationship relating shear and retention can be seen in Figure 29. This data was collected to match retention on the pilot fourdrinier machine used in Phase III to the dynamic retention/drainage jar used in Phase I. The graph shows the correlation to occur at approximately 300 rpm. More importantly, it shows the general shear/retention relationship. Retention starts very high in the 200 to 300 rpm range. As shear increases to 400-500 rpm, a rapid decrease in retention is apparent. It appears that a bonding energy threshold is reached beyond which shear forces dominate Van der Waal forces of attraction between particles and, therefore, retention shows a sharp decrease. When shear forces in the area of 700 rpm have been reached, retention levels off at approximately 32%. At this point, colloidal forces are at a minimum with this level of retention being attained primarily through the entrapment mechanism.

In this research project, shear was the variable showing the largest changes in retention with increasing levels. Phase I results showed decreases of up to 60% when increasing shear from 300 to 900 rpm. This was important to show how various commercial machines will respond under similar wet end conditions. However, on a particular machine, it will be the other variables which will determine the level of retention obtained.

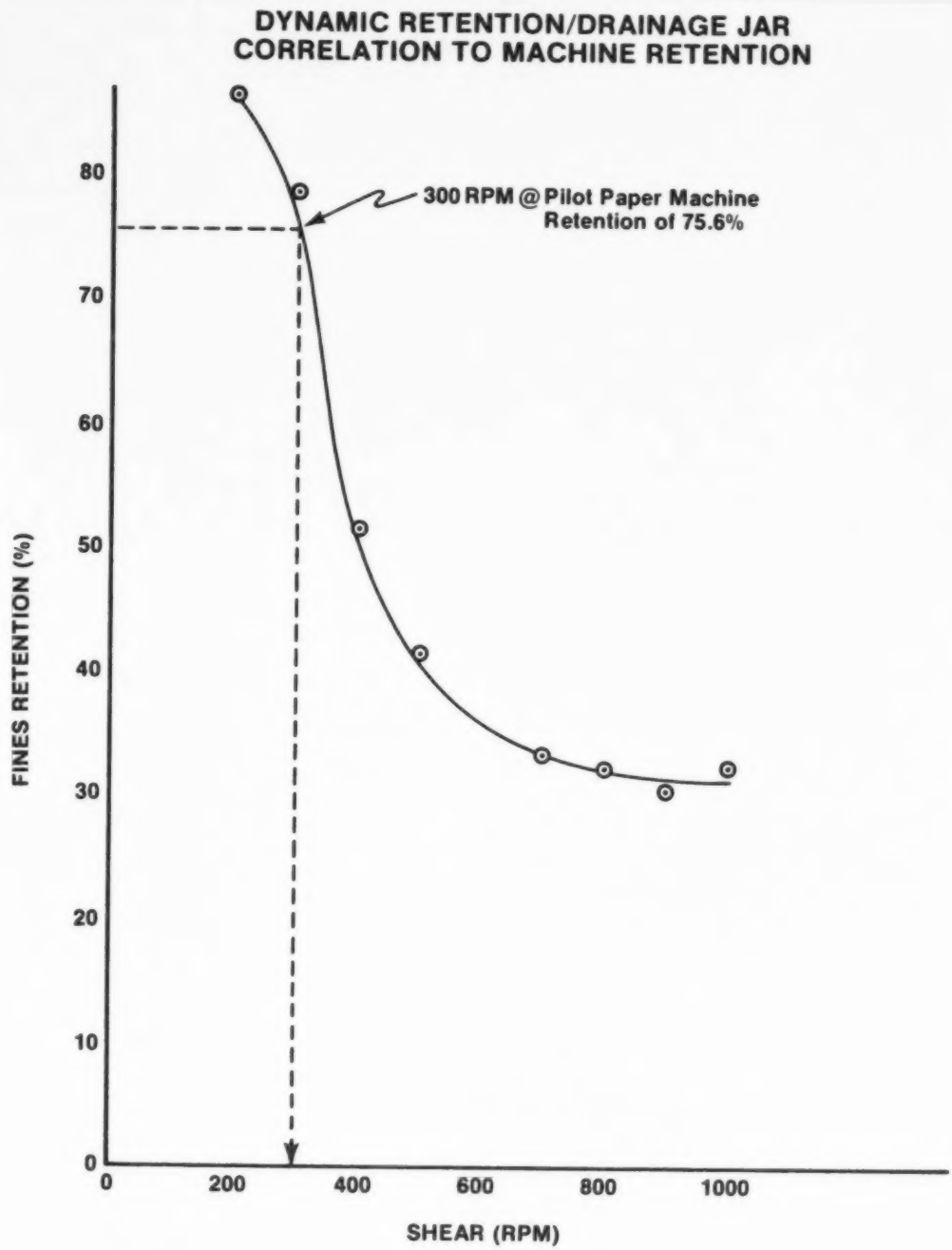


Figure 29. Retention vs. Shear

Effect of Alum

An investigation of the effects of alum and the necessity for alum control was the focal point of this research project. The results from Phases I and III confirm that alum control is desireable if retention is to be optimized.

Several important observations were made from the results of Phase I. First, alum is useful in overcoming the negative effect of anionic contaminants. These contaminants, mainly organic in nature, act to increase the amount of negative charge in the system and, thereby, increase the "cationic demand". Alum acts to contribute cationic charge; therefore, more alum is needed to neutralize the anionic contaminants and create conditions suitable for optimum coagulation (see Figure 17). Increasing alum from 1% to 3% improved retention 20% in a system containing high concentrations of anionic material. This has been recognized for controlling pitch problems where additional alum is added to coagulate and remove the anionic pitch particles (42). Alum control would, therefore, be required in a closed mill system where anionic contaminants would be likely to increase in concentration.

Secondly, high concentrations of alum did not cause dramatic decreases in retention in systems where polymer retention aids were not being used. It was originally suspected that as alum built up in the whitewater system, excessive positive charge would cause colloidally stable conditions and retention would suffer. However, the zeta potential studies concluded that, at pH 4.50, the system was electrokinectically buffered in the range where optimum coagulation occurs even at alum concentrations of up to 30% on fiber. According to electrokinetic theory, retention should not have suffered and this is exactly what happened. The slight decrease that did occur was probably due to a weakening of the alum floc between particles with increasing alum concentrations or by the fact that, during the retention measurements, the actual weight of alum in the sample is constantly increasing. With the large amounts of aluminum hydroxide, it is possible that the entrapment mechanism was adversely affected to some degree. These observations were confirmed both in Phase I using the dynamic retention/drainage jar and in Phase III during the 46 hour pilot paper machine trial. In both cases, polymer retention aids were not used.

Thirdly, in systems where high molecular weight cationic polymers are being used, high alum concentrations had a very detrimental effect on the ability of the polymer to improve retention. In fact, in studies on the paper machine and in the dynamic retention/drainage jar, optimum retention was achieved with no alum being used. As alum concentrations increased, retention steadily decreased. Also, in both cases, retention actually decreased to a point below the level in the system where no polymer was being used. The fact that retention decreases is not surprising since the polymer relies on anionic bonding sites on the fiber and fines. As alum concentrations increase, these bonding sites are taken by the aluminum ions and are, therefore, not available to the polymer. The situation then occurs where all the adsorption sites are

occupied by aluminum ions and the polymer in solution acts as a dispersing agent causing increased colloidal stabilization in the system and poorer retention. This is why retention fell to levels below those found in the system containing no polymer. The stabilization could not be confirmed with particle charge measurements; however, it is theorized that this may be a manifestation of the method of charge measurement and the high alum concentrations in the sample. Under the quiescent conditions found in the electrophoresis cell, the stabilization effect may be destroyed by the settling of the aluminum hydroxide floc.

It is interesting to note that the decrease in retention in the polymer studies was almost identical to the decrease in retention observed during the 1977 machine run at Miami University when comparing similar alum concentrations. It appears likely that it was this alum/polymer interaction which caused the observed decrease in retention during that run.

Effect of Organics

This variable had the largest effect on retention next to that of shear. At the concentrations used in Phase I, organics consistently decreased retention with increasing concentrations. This effect has been illustrated previously in the literature using extracted pure substances such as pine xylan or lignosulfonates. However, this study is the first to study the effect of organics in fine paper manufacturing using an organic concentrate actually derived from beating the virgin fiber used in the manufacturing process. An analysis of this concentrate is shown in Table 5.

The organic concentrate used in the study contained polysaccharides and organic acids having carboxyl groups which ionize when placed in water much in the same way that cellulose ionizes to become negatively charged. It is not surprising, then, that this organic concentrate had a cationic demand of approximately 2% alum for every 200 ppm of concentrate. This was found during the zeta potential studies of Phase I. The retention study results concluded that, by properly adjusting the alum concentration, the negative effects of the organic concentrate could be overcome. This is shown graphically in Figure 19 where increasing the alum concentration from 0% to 10% increased retention from 55% to 85%.

Effect of Inorganics

Of the chemical parameters investigated during this project, inorganics had the smallest effect on retention. The calcium, magnesium, manganese, and iron used to represent the inorganic fraction function much the same way as alum, i.e., by contributing positive charge to neutralize the negatively charged fiber and fines. The effect of these ions on retention basically followed electrokinetic theory. As shown in Figure 18, adding positively charged inorganic ions to a system exhibiting a positive zeta potential decreased retention. Adding inorganic ions would improve retention when high concentrations of organic contaminants are present, an effect also illustrated in Figure 18. The

consequences for a totally closed system are that possibly the build up of organic and inorganic contaminants may neutralize the negative effects exhibited by either one independent of the other. Wet end chemistry should be monitored, using charge measurements as an indicator, to understand the electrokinetic balance in the system prior to and after alum and rosin addition.

Effect of Polymer

An investigation of alum/polymer interactions was added to this research project because of the increasingly widespread use of polymer retention aids in the industry. Increasing machine speeds, the rapidly rising costs of raw materials, and more stringent environmental regulations have made filler losses through the wire and saveall system increasingly unacceptable. The results of Phase I and III show alum control becomes very important in systems using high molecular weight cationic polymers. The specifics of this interaction were discussed earlier in the "Effect of Alum" section.

Effect of Basis Weight

The 46 hour machine run, which was conducted during Phase III, showed striking differences to the 1977 machine run at Miami University with respect to retention. That is, retention did not decrease during this project as it had in 1977. It was suspected that the different basis weights used were responsible. Trials on the pilot paper machine proved that this was not the case. Over the range of basis weights studied, retention did not vary more than 10% for similar wet end conditions. The general trend was increasing retention with increasing basis weight. This agrees with the filtration theory of retention which states that retention depends upon the weight and thickness of the fiber mat. As basis weight increases, so also does the weight and thickness of the mat formed at the wet end. The difference in retention, however, was not very dramatic over the range studied during this project.

PHASE II - ALUM TITRATION METHOD INTERFERENCE ANALYSIS

The experiments carried out in Phase II were designed to test the hypothesis that the build up of dissolved solids in closed whitewater systems may cause interferences in this measurement technique. Inorganic chemical analyses from the 1977 machine trial at Miami University were used to establish the ions to be tested. The organic concentrate generated for Phase I was also tested. Interference from iron and the organic concentrate was determined to be 5 ppm and 24 ppm (as alum), respectively. The other metal ions exhibited no interference.

While interference to the alum titration method was determined, it does not preclude the use of this method in closed systems. The maximum predicted interference would result in an error of one half of one percent above the actual level of alum in the sample. Based on the retention analyses in Phases I and III, an error of this magnitude in an alum determination with subsequent dose rate adjustments would not cause a serious decrease in retention. Also, if the interference were known, corrections could be made to the alum determination to reflect the actual level of alum present.

In Phase III, the titration was used to measure alum concentrations in the stock chest, headbox, tray, silo, and saveall. The method proved to be a simple five minute procedure to accurately measure alum concentrations which occur in papermaking systems. An alum control strategy will be proposed which is based on the measurement of alum in the stock chest using this titration procedure.

AN ALUM CONTROL STRATEGY FOR TOTAL WATER REUSE

Based on information obtained from the literature and from the results of this study, an alum control strategy is proposed for totally closed whitewater systems in fine paper manufacture. This strategy has independent control of pH as an essential ingredient for successful wet end chemistry optimization. The literature supports this idea, citing poor sizing and deposit problems caused by the high acidity and high aluminum hydroxide formation from the overuse of alum. The use of an alternate acid, such as sulfuric acid, would avoid these problems. pH should be controlled for optimization of sizing, usually in the 4.5 to 5.5 range.

How alum is controlled depends on the type of system involved, i.e., whether it is a low shear or high shear system. It is proposed that alum be controlled for three purposes: to set the rosin size, to eliminate retention problems due to anionic contaminants, and to avoid retention problems associated with alum/polymer interactions. In either the low shear or high shear system, the amount of alum needed to set the rosin size should be the same and will depend on the concentration of rosin being used for a particular grade. The alum concentrations in the chest due to recirculation of whitewater should be monitored and only enough additional alum should be added for adequate sizing.

In low shear systems, alum acts to a limited extent as a retention aid. Figure 27 illustrates the characteristic alum vs. retention curve at low shear. Adding alum improved retention about 10% over using no alum at all on the pilot paper machine. However, in Figure 17, the effect of anionic contaminants is shown. These contaminants have the ability to decrease retention according to the amount present. Alum should be added at a rate sufficient to satisfy the cationic demand of these anionic contaminants as shown in Figure 21. This rate should be determined through zeta potential measurements. In addition, low shear systems will not require the use of polymer retention aids due to the high retention levels obtained with alum alone. Therefore, the negative effects due to alum/polymer interactions will not be present and will not need to be controlled. In short, alum control in low shear systems will involve adding the required amount of alum to set the rosin size and adding enough additional alum to satisfy the cationic demand of anionic contaminants in the system. Both of these determinations should be made on samples obtained from the stock chest prior to alum addition.

For high shear systems, control of alum becomes increasingly important due to alum/polymer interactions which cause decreases in retention. Figure 24 illustrates this effect. Most medium and high shear systems will require the use of polymeric retention aids to achieve satisfactory retention levels; therefore, control of alum concentrations will be critical. The effect of anionic contaminants on polymer effectiveness was not studied during this project; however, it was an area suggested for future work. Because of the negative effect of alum on polymer effectiveness, another chemical additive should be used to control any retention problems resulting from anionic contaminants. Low molecular weight cationic polyamines could possibly be used for this purpose. To summarize, in high shear systems, alum control will involve adding only enough alum to set the rosin size and avoiding alum build up which may cause severe retention problems due to alum/polymer interactions. By monitoring the amount of alum in the stock chest prior to any further additions, the proper alum dose rate can be determined.

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APPENDIX A

STATISTICAL ANALYSES
PHASE I - BENCH SCALE RETENTION ANALYSES

Experiment A - Yate's Algorithm

Trial	A	R	I	FPFR	(1)	(2)	(3)	D	Est.	ID
1	-	-	-	78.24	130.85	166.46	297.05	8	37.13	Ave
2	+	-	-	52.61	35.61	130.59	-45.17	4	-11.29*	A
3	-	+	-	20.67	96.19	-31.36	-157.03	4	-39.25*	R
4	+	+	-	14.94	34.40	-13.81	32.63	4	8.16*	AR
5	-	-	+	54.73	-25.63	-95.24	-35.87	4	-8.97*	I
6	+	-	+	41.46	-5.73	-61.79	17.55	4	4.39*	AI
7	-	+	+	17.47	-13.27	19.90	33.45	4	8.36*	RI
8	+	+	+	16.93	-0.54	12.73	-7.17	4	-1.79	ARI

*Significant Effect

Trial	Y_1	Y_2	d	$d^2/2$
1	82.36	74.11	8.25	34.03
2	17.87	17.07	0.80	0.32
3	52.39	52.83	0.44	0.10
4	50.53	58.92	8.39	35.20
5	15.23	14.64	0.59	0.17
6	20.24	21.09	0.85	0.36
7	40.46	42.46	2.00	2.00
8	12.04	21.82	9.78	47.82
			$d^2/2$	120.00

$S^2 = d^2/2g = 240/16 = 15$

$S = 3.87$

$4/16 \times 15 = 1.25$

Estimated Standard Error of Effect $= \sqrt{1.25} = 1.12$

$t_{0.05,13} = 2.16$

95% Confidence Limits = $1.12 \times 2.16 = \pm 2.42$

LEGEND

A - Alum
R - Revolutions Per Minute
I - Inorganics
FPFR - First Pass Fines Retention

Experiment B - Yate's Algorithm

Trial	A	O	I	FPFR	(1)	(2)	(3)	D	EST	ID
1	-	-	-	49.13	100.67	166.60	333.69	8	41.71	Ave
2	+	-	-	51.54	65.93	167.09	-11.05	4	-2.76*	A
3	-	+	-	34.48	94.26	-0.62	-56.17	4	-14.04*	O
4	+	+	-	31.45	72.83	-10.43	-2.43	4	-0.61	AO
5	-	-	+	50.49	2.41	-34.74	0.49	4	0.12	I
6	+	-	+	43.77	-3.03	-21.43	-9.81	4	-2.45	AI
7	-	+	+	38.27	-6.72	-5.44	13.31	4	3.33*	OI
8	+	+	+	34.56	-3.71	3.01	8.45	4	2.11	AOI

*Significant Effect

Trial	Y_1	Y_2	d	$d^2/2$	
1	47.82	50.83	3.41	5.82	$d^2/29 = 49.71/8 = 6.21$
2	36.70	32.34	4.36	9.51	
3	38.74	37.76	0.98	0.48	$S = 2.49$
4	49.19	53.89	4.70	11.05	
5	48.52	52.45	3.93	7.72	$4/16 \times 6.21 = 1.55$
6	32.28	30.53	1.75	1.53	
7	36.95	31.92	5.03	12.65	Estimated Standard
8	44.46	43.08	1.38	0.95	Error of Effect
			$d^2/2 =$	49.71	$= \sqrt{1.55} = 1.25$

$t_{0.05,13} = 2.16$
95% Confidence Limits = $1.25 \times 2.16 = \pm 2.70$

LEGEND
A - Alum
O - Organics
I - Inorganics
FPFR - First Pass Fines Retention

Experiment C - Regression Analysis

Variable No.	Identification
5	Inorganics
6	Organics
7	Alum
8	Inorganics^2
9	Organics^2
10	Alum^2
11	Inorganics/Organics
12	Inorganics/Alum
13	Organics/Alum
14	Inorganic/Organic/Alum

Variable	Correlation X VS y	Regression Coefficient	Standard Error Reg. Coef.	Computed T Value
5	0.0398	-0.0634	0.0344	-1.8415
6	-0.6059	-0.0248	0.0059	-4.1975*
7	0.3552	2.9924	4.4108	0.6784
8	0.0755	0.0002	0.0001	1.3728
9	-0.5906	-0.11E-05	0.34E-05	-0.3112
10	-0.3429	-0.6395	1.0372	-0.6165
11	-0.1610	0.15E-03	0.37E-04	3.9720*
12	0.0838	0.0032	0.0123	0.2591
13	-0.2940	0.0071	0.0021	3.3641*
14	-0.1167	-0.47E-04	0.17E-04	-2.7400*

The Dependent Variable is First Pass Fines Retention
Intercept 80.722
Multiple Correlation 0.92
Standard Error of Estimate 2.5407

ANALYSIS OF VARIANCE FOR THE REGRESSION

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Squares	F Value
Attributable to Regr.	10	571.75	57.175	8.86
Deviation From Regr.	16	103.28	6.4551	
Total	26	675.03		

$t_{0.05,\ 16} = 2.12$ *Significant Variables

Experiment D - Yate's Algorithm

Trial	A	O	I	FPFR	(1)	(2)	(3)	D	EST	ID
1	-	-	-	34.71	64.95	121.02	249.83	8	31.23	Ave
2	+	-	-	30.24	56.07	128.81	-1.01	4	-0.25	A
3	-	+	-	28.33	69.56	-5.06	-19.19	4	-4.80*	O
4	+	+	-	27.74	59.25	4.05	3.81	4	0.95	AO
5	-	-	+	33.75	-4.47	-8.88	7.79	4	1.95	I
6	+	-	+	35.81	-0.59	-10.31	9.11	4	2.28	AI
7	-	+	+	28.63	2.06	3.88	-1.43	4	-0.36	OI
8	+	+	+	30.62	1.99	-0.07	-3.95	4	-0.99	AOI

*Significant Effect

Trial	Y_1	Y_2	d	$d^2/2$
1	33.14	36.01	2.60	3.38
2	26.68	28.79	2.11	2.23
3	31.27	36.23	4.96	12.3
4	28.71	28.55	0.16	0.02
5	28.08	28.58	0.50	0.13
6	35.81	-----	----	-----
7	28.63	-----	----	-----
8	30.62	-----	----	-----
			$d^2/2$ =	18.06

$d^2/2g = 18.06/5 = 3.61$

$S = \sqrt{3.61} = 1.90$

$4/10 \times 3.61 = 1.44$

Estimated Standard Error of Effect = $\sqrt{1.44} = 1.20$

$t_{0.05, 10} = 2.23$

95% Confidence Limits = $1.20 \times 2.23 = \pm 2.68$

LEGEND

A - Alum
O - Organics
I - Inorganics
FPFR - First Pass Fines Retention

Experiment E - Yate's Algorithm

Trial	A	O	I	FPFR	(1)	(2)	(3)	D	EST	ID
1	-	-	-	23.07	49.47	96.05	187.75	8	23.47	Ave
2	+	-	-	26.40	46.58	91.70	-7.59	4	-1.90*	A
3	-	+	-	25.35	44.58	-0.79	-0.35	4	-0.09	O
4	+	+	-	21.23	47.12	-6.80	-13.77	4	-3.44*	AO
5	-	-	+	22.41	3.33	-2.89	-4.35	4	-1.09	I
6	+	-	+	22.17	-4.12	2.54	-6.01	4	-1.50*	AI
7	-	+	+	26.84	-0.24	-7.45	5.43	4	1.36	OI
8	+	+	+	20.28	-6.56	-6.32	1.13	4	0.28	AOI

*Significant Effect

Trial	Y_1	Y_2	d	$d^2/2$
1	19.87	20.69	-0.82	0.37
2	22.62	23.51	-0.89	0.40
3	22.77	19.69	3.08	4.74
4	27.33	26.35	0.98	0.48
5	25.53	25.17	0.36	0.06
6	22.89	21.44	1.45	1.05
7	25.25	27.55	-2.30	2.65
8	20.28	-----	-----	-----
			$d^2/2 =$	9.75

$d^2/2g = 9.75/7 = 1.39$

$S = \sqrt{1.39} = 1.18$

$4/14 \times 1.39 = 0.40$

Estimated Standard Error of Effect = $\sqrt{0.40}$

$= 0.63$

$t_{0.05, 12} = 2.18$

95% Confidence Limits = $0.63 \times 2.18 = \pm 1.37$

LEGEND

A - Alum
O - Organics
I - Inorganics
FPFR - First Pass Fines Retention

PHASE II
ALUM TITRATION METHOD
INTERFERENCE ANALYSIS

Organic Concentrate

	Volume Titrant Required			
	Y_A (with organics)	Y_A^2	Y_B (without organics)	Y_B^2
	0.85	0.7225	0.75	0.5625
	0.87	0.7569	0.70	0.4900
	0.89	0.7921	0.76	0.5776
	0.86	0.7396	0.76	0.5776
	0.89	0.7921	0.70	0.4900
Sum	4.36	3.8032	3.67	2.6977
$\bar{y}$	0.872		0.734	

$\bar{Y}_B - \bar{Y}_A = 0.138$

$Y_B^2 - (\Sigma Y_B)^2/n_B = 2.6977 - \frac{13.4689}{5} = 0.00392$

$Y_A^2 - (\Sigma Y_A)^2/n_A = 3.8032 - \frac{19.0096}{5} = 0.00128$

Pooled Estimate of σ^2 $\quad S^2 = \frac{0.00128 + 0.00392}{8} = 0.00065$

Standard Error $= \sqrt{\frac{25^2}{5}} = 0.0161245$

$t_o = \frac{0.138}{0.0161245} = 8.55 \quad \nu = 8$

Pr ($t \geq 8.55$) = less than 0.001 - therefore, means are statistically different

Iron

	Volume Titrant Required			
	Y_A (with Fe)	Y_A^2	Y_B (without Fe)	Y_B^2
	0.83	0.6889	0.78	0.6084
	0.85	0.7225	0.77	0.5929
	0.80	0.6400	0.80	0.6400
	0.82	0.6724	0.80	0.6400
	0.80	0.6400	0.78	0.6084
Sum	4.10	3.3638	3.93	3.0897
$\bar{Y}$	0.82		0.786	

$Y_A^2 - (\Sigma Y_A)^2/n_A = 0.0018$

$Y_B^2 - (\Sigma Y_B)^2/n_B = 0.00072$

$\bar{Y}_A - \bar{Y}_B = 0.034$

Pooled Estimate of σ^2 $\quad S^2 = \frac{0.0018 + 0.00072}{8} = 0.000315$

Standard Error $= \sqrt{\frac{25^2}{5}} = 0.011225$

$t_o = \frac{0.034}{0.011225} = 3.03$ with $\nu = 8$

Pr ($t \geq 3.03$) = greater than 95% confidence;
therefore, means are statistically different

Calcium

	Volume Titrant Required			
	Y_A (with Ca)	Y_A^2	Y_B (without Ca)	Y_B^2
	0.80	0.6400	0.80	0.6400
	0.83	0.6889	0.80	0.6400
	0.83	0.6889	0.84	0.7056
	0.80	0.6400	0.80	0.6400
	0.82	0.6724	0.80	0.6400
Sum	4.08	3.3302	4.04	3.2656
$\bar{Y}$	0.816		0.808	

$\bar{Y}_B - \bar{Y}_A = 0.008$

$Y_B^2 - (\Sigma Y_B)^2/n_B = 3.2656 - \frac{16.3216}{5} = 0.00128$

$Y_A^2 - (\Sigma Y_A)^2/n_A = 3.3302 - \frac{16.6464}{5} = 0.00092$

Pooled Estimate of σ^2 $\quad S^2 = \frac{0.00128 + 0.00092}{8} = 0.000275$

Standard Error $= \sqrt{\frac{25^2}{5}} = 0.0104881$

$t_o = \frac{0.008}{0.0104881} = 0.7627692 \quad \nu = 8$

Pr ($t \geq 0.76$) = 0.25 - therefore, means are not statistically different

Magnesium

	Volume Titrant Required			
	Y_A (with Mg)	Y_A^2	Y_B (without Mg)	Y_B^2
	0.77	0.5929	0.75	0.5625
	0.82	0.6724	0.76	0.5776
	0.78	0.6084	0.77	0.5929
	0.80	0.6400	0.80	0.6400
	0.80	0.6400	0.80	0.6400
Sum	3.97	3.1537	3.88	3.0130
$\bar{Y}$	0.794		0.776	

$$\bar{Y}_A - \bar{Y}_B = 0.018$$

$$Y_A^2 - (\Sigma Y_A)^2/n_A = 3.1537 - \frac{15.7609}{5} = 0.00152$$

$$Y_B^2 - (\Sigma Y_B)^2/n_B = 3.01030 - \frac{15.0544}{5} = 0.00212$$

Pooled Estimate of σ^2 $\quad S^2 = \frac{0.00152 + 0.00212}{8} = 0.000455$

Standard Error - $\sqrt{\frac{25^2}{5}} = 0.0134907$

$$t_o = \frac{0.018}{0.0134907} = 1.33 \quad \nu = 8$$

Pr ($t \geq 1.33$) = 0.10 - therefore, means are not statistically different

Manganese

	Volume Titrant Required			
	Y_A (with Mn)	Y_A^2	Y_B (without Mn)	Y_B^2
	0.80	0.6400	0.75	0.5625
	0.74	0.5476	0.77	0.5929
	0.79	0.6241	0.79	0.6241
	0.75	0.5625	0.78	0.6084
	0.80	0.6400	0.78	0.6084
Sum	3.88	3.0142	3.87	2.9963
$\bar{Y}$	0.776		0.774	

$$\bar{Y}_B - \bar{Y}_A = 0.002$$

$$Y_B^2 - (\leq Y_B)^2/n_B = 2.9963 - \frac{14.9769}{5} = 0.00092$$

$$Y_A^2 - (\leq Y_A)^2/n_A = 3.0142 - \frac{15.0544}{5} = 0.00332$$

Pooled Estimate of σ^2 $\quad S^2 = \frac{0.00332 + 0.00092}{8} = 0.00053$

Standard Error $= \sqrt{\frac{25^2}{5}} = 0.0145602$

$$t_o = \frac{0.002}{0.0145602} = 0.137 \quad \nu = 8$$

Pr ($t \geq 0.137$) = 0.40 - therefore, means are not statistically different

APPENDIX B

QUANTITATIVE DETERMINATION OF ALUM

Materials

Apparatus includes an expanded scale pH meter, a fluoride selective-ion electrode, a 10-ml plastic buret, and a magnetic stirrer.

Reagents

0.1M sodium fluoride (4.2g of NaF/liter of distilled water), and a 3.8 pH buffer (1.2 moles of glacial acetic acid, 0.96 moles of sodium perchlorate, 0.24 moles of sodium acetate/liter of distilled water). The ingredients for one liter of pH buffer in grams are: 72g glacial acetic acid (or 68.6 ml), 134.84g sodium perchlorate, and 19.70g sodium acetate.

Procedure

1. Calibrate the pH meter and fluoride electrode according to the manufacturers instructions.

2. Determine the titration end point. Add 0.1 ml of 0.1M NaF solution to a 200 ml beaker containing 100 ml of distilled water and 5 ml of 3.8 pH buffer. Agitate well with a magnetic stirrer and measure the potential with the fluoride electrode. This potential is designated as the "end point" for all subsequent titrations. Any changes in NaF concentration, sample size, or amount of buffer added will necessitate a new end point determination. The end point should be about +80 MV, although the potential may vary somewhat from this value.

3. Determine the blank correction. Add 5 ml of 3.8 pH buffer to 100 ml of distilled water in a 200 ml beaker. Agitate well with magnetic stirrer. Titrate with 0.1M NaF solution until the end point is reached and held for a minimum of 30 seconds. Record the volume required. This value is the blank correction to be used in the following steps.

4. Determine the alum concentration in a sample. Add 100 ml of sample to a 200 ml beaker containing a magnetic stirring bar. Add 5 ml of 3.8 pH buffer. Activate the magnetic stirrer and place fluoride electrode in the sample. Using a 10 ml buret, titrate with 0.1M NaF to the predetermined end point making sure that the end point potential is maintained for a minimum of 30 seconds. Correct the volume of titrant required by subtracting the blank correction. The alum concentration can be read from an alum calibration curve developed by titrating samples containing known concentrations of alum.